U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-253 648

THE SORPTION OF PLUTONIUM ON MINERALS AND SEDIMENTS

PITTSBURGH UNIVERSITY

PREPARED FOR
DEPARTMENT OF HEALTH, EDUCATION AND WELFARE

AUGUST 1967

173093

PB 253 648

COMPREHENSIVE PROGRESS REPORT
To
The Division of Radiological Health, PHS

THE SORPTION OF PLUTONIUM ON MINERALS AND SEDIMENTS

Covering the Period
June 1, 1966 to August 31, 1967

By
J. B. Andelman, Ph. D., Principal Investigator
and
T. C. Rozzell, M. S., Research Assistant

August, 1967

DEPARTMENT OF PUBLIC HEALTH PRACTICE
GRADUATE SCHOOL OF PUBLIC HEALTH
UNIVERSITY OF PITTSBURGH
PITTSBURGH, PENNSYLVANIA 15213

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

THE SORPTION OF PLUTONIUM ON MINERALS AND SEDIMENTS

Covering the Period

June 1, 1966 to August 31, 1967

Research Grant No. 2 R01 RH 00322-03

Prepared for

THE DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
BUREAU OF STATE SERVICES
DIVISION OF RADIOLOGICAL HEALTH

By

Julian B. Andelman, Ph.D., Principal Investigator

and

Thomas C. Rozzell, M.S., Research Assistant

Environmental Health Section
University of Pittsburgh
Graduate School of Public Health
Pittsburgh, Pennsylvania 15213

August, 1967

ABSTRACT

The rate of sorption of aqueous plutonium onto the surface of crystalline quartz (silica) has been studied as a function of age of the plutonium solution, pH, the amount of plutonium presorbed, silica particle size and the temperature of formation of the plutonium hydrolysis products. Particle sizes of aggregates of the plutonium hydroxide precipitates and polymers have been determined by filtration and correlated with centrifugation studies. A direct method of determining the amount of plutonium sorbed on silica has been developed. Different types of silica have been characterized. Desorption rates of plutonium from silica were investigated, both as a function of pH and age of the sorbed plutonium.

TABLE OF CONTENTS

Section		Page No.
	ABSTRACT	ii
	LIST OF TABLES	iv
	LIST OF FIGURES	v
I.	INTRODUCTION	1
II.	RESEARCH PLAN	7
III.	RESULTS AND DISCUSSION	9
	A. Chemical and Physical Properties of Plutonium in Aqueous Solution	9
	B. Sorption of Plutonium onto Silica	23
	1. Method of Analysis	23
	2. Sorption as a Function of Age of the Plutonium Solution	24
	3. Sorption as a Function of pH	25
	4. Sorption as a Function of the Amount of Plutonium Presorbed	28
	5. Sorption as a Function of Silica Particle Size	30
	6. Sorption as a Function of Temperature During Hydrolysis	33
	C. Desorption of Plutonium from Silica	33
	1. Desorption in a Limited Volume Solution	33
	2. Effect of pH on Pu (IV) Desorption	35
	3. Desorption of Fresh and Aged Plutonium	37
	D. Characterization and Properties of Silicas	41
	1. Silica Surface Area and Particle Size	42
	2. Determination of Silica in an Aqueous Medium	45
IV.	SUMMARY AND CONCLUSIONS	49
V.	FUTURE WORK	52
VI.	REFERENCES	54

LIST OF TABLES

Table No.		Page No.
I.	DESORPTION CONSTANTS	40
II.	"BOND" SILICA SIZE DISTRIBUTION..	44
III.	COMPARISON OF MIN-U-SIL SURFACE AREAS.....	44

LIST OF FIGURES

Figure No.		Page No.
1	Pu (IV) Aggregate Size Distribution.....	12
2	Filterability of Pu (IV) Aggregates.....	14
3	Sorption of Pu by Soil as a Function of pH (After Rhodes)	17
4	Centrifugability of Pu (IV) Aggregates @ pH 7.....	19
5	Centrifugability of Pu (IV) Solutions of Different Ages.	20
6	Sorption of Pu (IV) by Soil as a Function of Time (After Rhodes).....	22
7	Sorption of Pu (IV) as a Function of Age of the Plutonium Solution.....	26
8	Effect of pH on Sorption of Pu (IV).....	27
9	Effect of Presorbed Pu (IV) on Subsequent Sorption.....	29
10	Effect of Silica Particle Size on Pu (IV) Sorption.....	31
11	Effect of Temperature During Hydrolysis on Sorption.....	34
12	Desorption of Pu (IV) in a Limited Volume Solution.....	36
13	Effect of pH on the Rate of Desorption.....	38
14	Rate of Desorption of Fresh and Aged Pu (IV).....	39
15	Min-u-Sil Particle Size Distributions.....	43
16	Noncentrifuged Silica vs Silica Particle Size.....	47
17	Relationship Between Non-centrifuged Silica and Centrifuge Speed.....	48

I. INTRODUCTION

The fate of radioactive contaminants of surface and ground waters has important ramifications for the public health. At the present time many radionuclides are routinely released to the aqueous environment in large volumes of low-level, liquid wastes, both from research and power reactors. Among these radionuclides are the very hazardous alpha-emitting isotopes of such elements as polonium, actinium, uranium, and plutonium (1).

Several studies (2-7) have been concerned with the presence of the more prevalent products of fission and neutron activation (i.e., such isotopes as ^{106}Ru-^{106}Rh, ^{137}Cs-^{137}Ba, ^{95}Nb, ^{90}Sr, etc.) in natural waters and their sorption by minerals and uptake by plants and marine life. However, there are relatively few such investigations of the heavier elements (atomic number greater than 82) associated with the normal operation of nuclear reactors.

Nuclear reactor operations give rise to three main types of wastes. If water is used as the coolant, activation products are produced from the elements present in the water. With single pass coolants, this may result in activity of the order of a picocurie per milliliter. With recirculating systems, small volumes of highly concentrated wastes are produced and are usually stored. The second source of wastes from reactor operations is the research laboratory and its associated laundry and decontamination wastes which usually are at a low level of activity. Finally, there are the wastes resulting from the reprocessing of spent fuel; these contain the major portion of the fission products produced in the reactor.

McKay (8), in an analysis of the hazards of the alpha emitters from reactor operations, points out that the most significant and hazardous species are plutonium, americium, curium, and neptunium. Plutonium is as hazardous as such fission products as ruthenium-106, cesium-137, cerium-144, and promethium-147, depending on the kind of fuel, the power of the reactor, the storage time of the waste and whether it is released by air or water. If strontium-90 is removed from the wastes, in several cases, particularly for wastes released to the air, plutonium becomes the most hazardous radionuclide.

When plutonium and other radioisotopes are released to surface or ground waters, it is possible that they may be concentrated by and in plants and on silt, sediments and other deposited and suspended materials in the water. It has been pointed out (5) that the concentration of radioisotopes on sediments or in aquatic organisms frequently exceeds that in the water, in some cases by several orders of magnitude. It is this concentration of the radioisotopes which poses one of the greatest problems in the management of low-level radioactive wastes. The radioisotopes, having been so concentrated, may be released suddenly at some future time in quantities far exceeding their maximum permissable concentrations.

The principal mechanisms involved in the concentration of radioisotopes onto minerals and sediments in natural waters are "adsorption" and "absorption". The former term refers to physical and chemical interactions between the surface of the solid and the solution species, while the latter involves the incorporation of the radioisotope into the bulk of the solid. The more general term "sorption" will be used to encompass both phenomena. Sorption from solution frequently leads to layers only one molecule thick, although

multilayer sorption has also been observed (9). In the case of monolayer sorption there is usually competition between solute and solvent for the surface of the solid. Ordinarily the solute-sorbate interactions, although strong enough to compete favorably with solvent in the first layer, do not do so in succeeding layers.

If the sorbing species is present in solution as an uncharged species, physical sorption may occur as a result of van der Waals forces. If the sorbing species is present as an ion or other charged species and the solid surface has ions of the same sign, ion exchange, which is a type of chemisorption, may take place. The ions in solution displace ions present on the surface or within the solid. This phenomenon may also occur for a species in solution that is uncharged or with a charge opposite to that of the ion with which it is exchanging on the surface. This can occur because a sorbing metal complex can change the sign of its charge when ligands are changed or lost.

In addition to specific interactions between the sorbing species and the surface, there may also be concentration of the charged species in the electric double-layer at the mineral solution interface. Such an interaction is highly influenced by the magnitude of the charge of the sorbing species, the ionic strength and ionic composition of the solution, and the double-layer potential.

When the sorbing species is a polymer, the latter may be held at one or several sites on the solid. It is known that plutonium exists as a polymer at low hydrogen ion concentrations where this type of sorption may be exhibited. At low pH the plutonium species range from neutral to highly-charged. Thus it is expected that each of the sorption phenomena mentioned will occur in varying degrees as the ambient solution conditions are varied.

Competition between solute and solvent for the surface sites of a solid is an important factor when solute concentration is high. However, in extremely dilute solutions, such as those encountered in most low-level, radioactive waste liquids, sorption of the solvent has only a negligible effect upon sorption of the solute.

Probably the single most important sediment characteristic affecting the extent of sorption is particle size. When surface interactions predominate, the sorption capacity of stream sediments is inversely proportional to the size of the particles. Thus, for a given weight or concentration of spherical sediment particles, the total surface area of one micron clay is 1,000 times greater than that for one millimeter sand. Ion exchange phenomena are generally associated with the fine-grained, expanding lattice clay minerals. Ion exchange occurs to some extent with larger grained sediments; however, exchange capacity diminishes rapidly as particle size increases.

The chemical and mineralogical nature of sediments, particularly of clays, is also important in determining the extent of sorption. The cation-exchange capacity (CEC) of the clay and the position of the adsorbed cations in the Hofmeister ion series* with respect to that of the radioactive cations in solution are also significant factors in this regard.

---

*A series expressing the relative bonding energies of some common exchangeable cations, e.g.,

$$Cs^{+} > Rb^{+} > K^{+} > Na^{+} > Li^{+}$$

for monovalent cations, and

$$Ba^{++} > Sr^{++} > Ca^{++} > Mg^{++}$$

for divalent cations.

The concentration of radioisotopes in the waste effluent or the receiving stream is an important factor in determining the amount of radioactivity which is sorbed by stream sediments. Waste effluent and stream water must be considered together, because it is the mixture of the two which determines the characteristics of the solution in the sorption system. Any one of a number of chemical characteristics of the waste-effluent-stream solution may radically alter the complexion of the entire sediment-solution sorption system. The presence in the solution of competing nonradioactive substances may greatly reduce the uptake of radioactivity by sediments. In streams, such nonradioactive substances might originate from other types of industrial wastes or from natural sources.

It has been shown that the extent of sorption may be greatly influenced by the effect of the pH of the solution on the ionic forms in solution. Changes in the pH of the solution may change the nature of the sorbing species as a result of a change in oxidation state, hydrolysis or polymerization. In addition, the nature of the double-layer at the mineral-solution interface (e.g., the charge, potential and thickness) is affected by pH, particularly for hydrated oxides like silica. Thus, changes in pH may seriously affect solute-surface interactions for a variety of reasons.

It is apparent from the foregoing discussion that the factors influencing the uptake of radioactivity by sediments are many and varied. In natural streams the sorption systems are further complicated by the fact that many factors will normally be operating simultaneously, thereby obscuring simple cause and effect relationships. A great deal of additional research and information is thus necessary in order to establish adequate criteria for predicting the extent to which sorption of radiocontaminants by sediments may occur in natural streams.

Of particular interest are the interactions between aqueous dissolved and colloidal plutonium species and mineral surfaces in soils and natural waters. Rhodes (10) has studied the sorption of plutonium by a subsurface soil in the vicinity of the hanford plant. He characterized the soil as to the nature of the mineral components and their particle size, but did not determine the relative sorption of plutonium on the different components. The pH, time of contact, and certain complexing anions were found to have a significant effect on the extent of sorption, which in some cases appeared to approach one hundred percent. It was also noted that the plutonium was not easily extracted once sorbed. Christenson, et al (11) studied the sorption of plutonium by a core of soil tuff taken from the Los Alamos area and found that when tap water from that area was spiked with plutonium and passed through a column of this material, it was sorbed at the top and was not removed appreciably by salt solutions containing sodium, calcium and magnesium. However, they found that solutions containing complexing agents and soaps affected the retention of plutonium on the tuff.

Jacobson and Overstreet (12) found that although the plutonium may in most instances be tightly held by soil components, between 19 and 94 percent of it in different oxidation states was taken up by barley plants grown in a bentonite suspension on which plutonium was sorbed. The activity was taken up by the roots and translocated in smaller amounts to the leaves. This could not have been accounted for by adherence of clay particles to the roots and vividly demonstrates the transfer of plutonium fixed on a soil mineral, to a plant.

The sorption of plutonium on quartz and on glass was studied by Samartseva (13) and King (14). The former found that in the concentration range of 10^{-8} to 10^{-10}M, plutonium had a sorption peak in the vicinity of pH 2.8 to 3.6, with decreasing but significant amounts being sorbed in the pH range of 4 to 11. Plutonium sorbed from a solution of pH greater than 4 was difficult to remove.

King studied the sorption of plutonium on glass and found, at trace concentrations, that the sorption increased as the hydrogen ion concentration decreased. This suggested that it is the colloidal form of plutonium which is preferentially sorbed. This was further shown to be the case by Carniglia (15) working with macro concentrations of plutonium.

Plutonium (IV) sorption onto materials such as glass, stainless steel, polyvinyl chloride (PVC) and gold has been studied by Haissinsky and coworkers (16, 17). In their work the Pu (IV) was in either sulfuric or nitric acid medium. It was found, for example, that the sorption in nitric acid onto platinum, gold, stainless steel and PVC increased with decreasing acidity.

In summary, the sorption of aqueous plutonium onto mineral surfaces in contact with natural waters has not been studied in depth. In particular the nature of the plutonium species, their charge, oxidation state, and state of polymerization in such waters needs further elucidation in order to understand their interactions with such minerals.

II. RESEARCH PLAN

The aim of this investigation is to study the kinetics and equilibria of the sorption of plutonium on mineral surfaces and the way in which they are affected by such variables as mineral particle size and nature, pH, ionic strength, nature of the ions in solution, temperature, oxidation state and the colloidal and ionic nature of the plutonium in solution. Since the end result of most sorptive processes is eventual desorption, the kinetics and the extent of desorption will also be studied. The desorption study is

particularly germane to the question of the fate of plutonium. It is desirable to know, once it is sorbed by minerals, to what extent and under what conditions will it be released.

It is expected that both colloidal and ionic sorption will be encountered (10, 18-20), and that the type of mineral used will have a significant effect on the sorption process. The elucidation of the specific mechanisms with specific minerals will contribute information that will aid in the prediction of the fate of plutonium as seasonal and other variations occur in natural waters. In addition, it is hoped that this information will be useful in controlling this potentially dangerous material and removing it by water and waste treatment processes.

The initial phases of this research have involved the interactions between aqueous plutonium and silica, one of the most prevalent minerals found in nature. Concentrated acid solutions of plutonium (IV) salts were diluted and buffered to pH values of natural waters (pH 3 to 8), where redox disproportionation reactions are encountered, as well as polymerization and colloidal formation. These plutonium solutions have been aged and characterized as to particle size distribution, using both centrifugation and membrane and other filtration techniques. The variables in studying the aging process have been temperature, pH, and the presence of silica particles (the latter here being considered as a possible catalytic surface affecting the plutonium aging process).

Silica particles of a variety of sizes and size distributions have been utilized in studying the interaction with plutonium. These silica samples have been characterized as to particle size distribution, and also separated into fractions with narrower size ranges. This has been done in order to study the effect of mineral particle size on the interaction with plutonium.

Techniques have been developed to separate the aqueous plutonium from the silica in order to determine the extent of sorption. Because of the polymerization and relative insolubility of plutonium hydroxide, the plutonium species encountered is frequently of the same order of size as the silica particles utilized.

The sorption of plutonium onto silica will be studied under a variety of conditions of solution composition associated with natural waters. Both the equilibria and rate of sorption have been studied, with emphasis on the age of the plutonium solution and the size of the silica particles. The rate of desorption at various values of solution pH has also been investigated.

III. RESULTS AND DISCUSSION

This section will include the results of this investigation and their discussion in relation to other published research. Where appropriate for background purposes, detailed discussions of such research will be presented, particularly in the following sub-section on the properties of aqueous plutonium.

A. Chemical and Physical Properties of Plutonium in Aqueous Solutions

Compounds of bivalent plutonium, Pu (II), have not been found in aqueous solutions due to rapid oxidation to Pu (III) with the simultaneous reduction of hydrogen ions.

Trivalent plutonium, Pu (III), appears in many compounds. It also occurs as the Pu (III) ion which is relatively stable in solutions of medium acidity (21). It has been shown (22) that acid solution hydrolysis of Pu (III) is negligible because of the relatively small value of the hydrolysis

constant* which is approximately 10^{-7} in chloride and perchlorate (23), and that Pu (III), like the tripositive rare earths, does not appear to have a strong tendency to form complex ions. Indeed, it has been found (24) that only very minor changes occur in the absorption spectra of solutions of Pu (III) in perchloric, nitric, hydrochloric and sulfuric acids as the concentrations of the anions are increased. This is further evidence that the complex-forming tendency of the Pu (III) ion is very low. At a pH of about 7, however the first small quantities of the hydrolysis product $Pu(OH)^{++}$ appears, and, at only slightly higher pH, either basic salts or the hydroxide, $Pu(OH)_3$, precipitates and extensive oxidation to $Pu(OH)_4$ occurs (25).

Concentrated aqueous solutions of Pu (III) are blue and the chemical properties of Pu (III) are similar to those of the rare earth metals which appear in the trivalent forms. This is apparently the result of their similarity in electrical charges, ion radii and structure of electron shells. Pu (III) may be absorbed by ion exchange resins only in the form of a cation, i.e., only on cation-exchange resins (21).

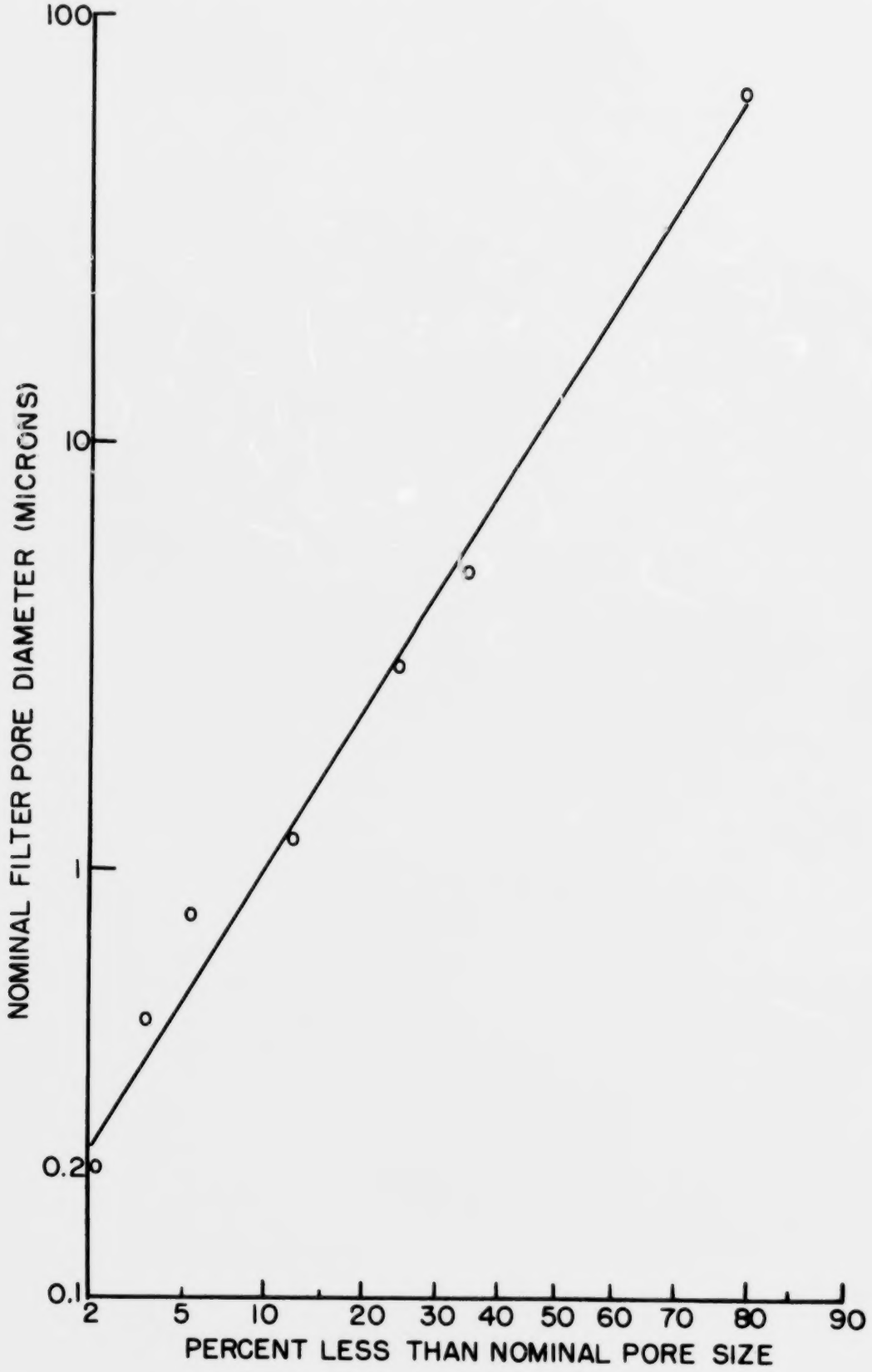
Tetravalent plutonium, Pu (IV), is known in many states in aqueous solutions. Pu (IV) is believed to exist in aqueous solutions of about 0.1M hydrogen ion concentration or greater as unhydrolyzed Pu(IV) (19), or some complex ion of Pu (IV), depending on the anions present. It appears to be uncomplexed in perchloric acid and in dilute HCl solutions. It is complexed by nitrate ion and by chloride ion at high concentrations and is strongly complexed by sulfate ions. The tetravalent state is the most prevalent oxidation state and is thus the initial state chosen in this research. It may be maintained as the sole oxidation state by holding the nitrate ion concentration high and the pH low.

---

*For the reaction: $Pu(OH)_x^{+3} + H_2O \rightleftarrows Pu(OH)_{x+1}^{+2} + H_3O^+$

Near pH 1 Pu (IV) begins to hydrolyze appreciably (20, 25), forming $Pu(OH)^{+3}$ and, possibly near pH 1.5, a considerable quantity of $Pu(OH)_2^{+2}$. Rapid polymerization, or the joining together of the hydroxides, begins to take place in the region pH 1 to 2, and Pu (IV) assumes a composition which for all intents and purposes can be considered to be that of $Pu(OH)_4$. The polymer presumably forms with oxygen or hydroxyl bridges for connection (26). The pH at which polymerization takes place is dependent upon the concentration of Pu (IV) (25). Above a pH of about 3 to 3.5 the majority of the plutonium is precipitated as the insoluble hydroxide $Pu(OH)_4$ (21). The actual ratio of hydroxide molecules to Pu ions is believed to approach 4 at the point where precipitation occurs. The solubility product of $Pu(OH)_4$ is estimated as $[Pu^{+4}]\ [OH^-]^4 = 7 \times 10^{-56}$ (21), which expresses the extreme insolubility of the Pu (IV) hydroxide.

During and following the hydrolysis of Pu (IV), polymeric aggregations of plutonium hydroxide are formed. These may be of the dimensions of radiocolloids formed in the manner described by Schubert (27); but since a radiocolloid is still generally thought to require an impurity as a nucleus for its formation, the term "plutonium aggregate" will be used to describe the Pu (IV) hydrolysis product, including both the precipitate of $Pu(OH)_4$ and the polymeric species. This research has shown that the size of these plutonium aggregates varies considerably in each solution in which they are formed. A typical size distribution curve is shown in Figure 1. This distribution was obtained by filtering an aged Pu (IV) solution of pH 7 through metal membrane filters and porous silica discs of various nominal pore diameters. The solution used was prepared by first converting all the plutonium to the tetravalent oxidation state with concentrated nitric acid. It was then titrated to approximately pH 7 with NaOH after dilution with water.



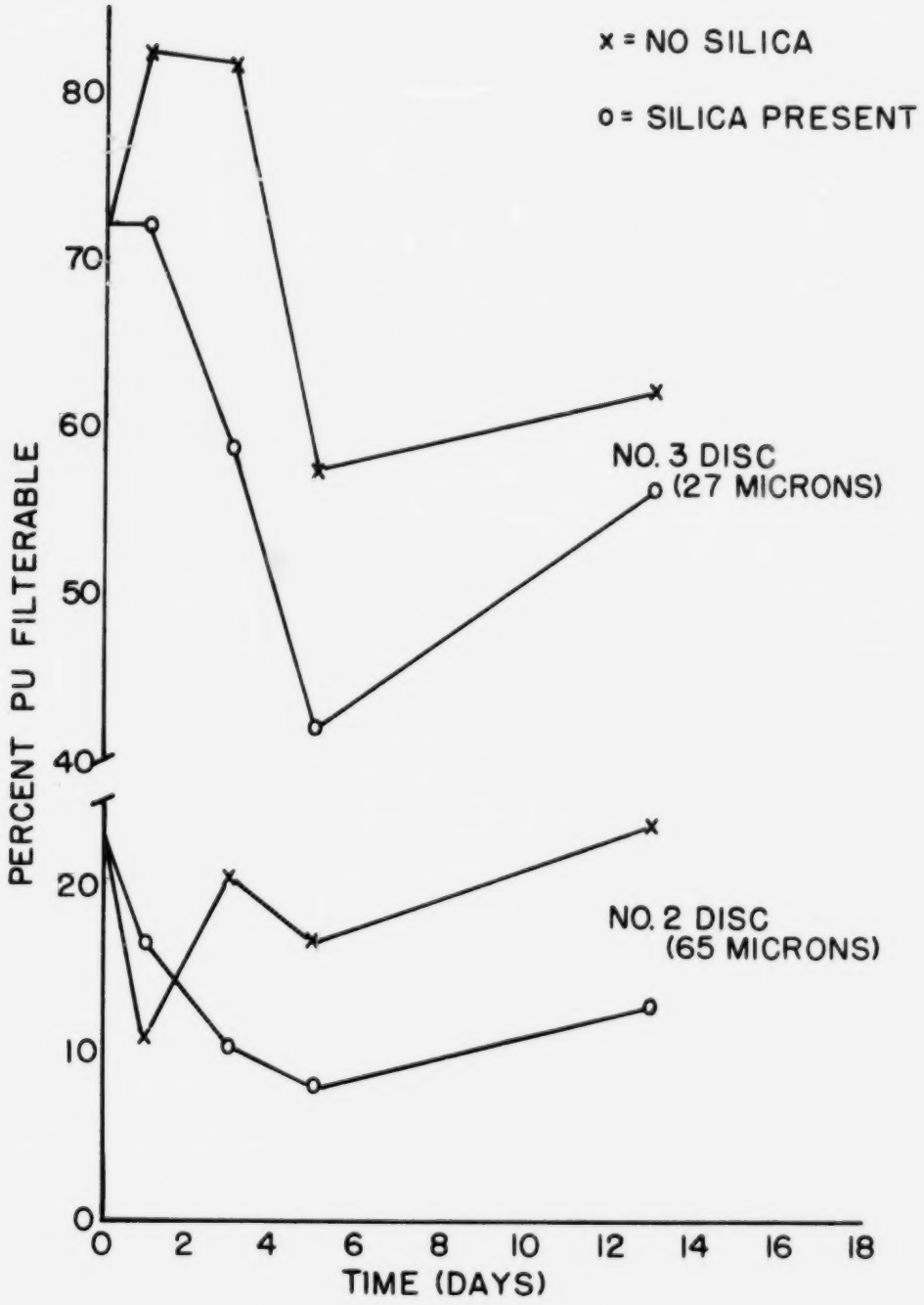
SIZE DISTRIBUTION OF Pu(IV) AGGREGATES
FIGURE 1

Phosphate buffer was added for pH stabilization. The solution was then allowed to age, while shaking, for four days. Separate aliquots were taken for each filtration. It is possible that there was some sorption by the filters but, due to the short contact time, this is believed to be minimal. A significant amount of material smaller than the nominal pore size is apparently trapped by the filters. This curve must not, therefore, be considered as giving anything more than the general shape of the true size distribution.

Relatively little information has been found concerning specific determinations of the size of the Pu (IV) polymer. Grebenshchikova and Davydov (19) gave some evidence of sizes. In their centrifugation and ultrafiltration experiments they found that approximately six percent of the colloid was less than 1-3 mμ and approximately 90 percent was greater than 30-40 mμ There is no way of determining how much greater than 30-40 mμ the material might have been.

The size distribution of the aggregates is greatly dependent upon the rate at which the polymer is formed, the plutonium concentration, the age of the plutonium solution, the incremental hydroxide ion concentration added in titrating, the presence or absence of complexing agents and the final pH of the solution (25).

The filterability (size) of the plutonium aggregates remaining in the bulk solution has been studied here as a function of time both in the presence and in the absence of silica, aged (32 day) plutonium being used in both cases. It was found, Figure 2, that a higher percentage of the plutonium which remained in the solution in the absence of silica was filterable than in the solution in which sorption onto silica was occurring. It is evident from this that the plutonium which is preferentially sorbed onto silica is large in size. The nominal pore diameters of discs two and three are 65 and 27 microns, respectively.



FILTERABILITY OF Pu(IV) AGGREGATES

FIGURE 2

The plutonium aggregates vary in weight as well as size (28, 20). It has been found that heating the plutonium solutions causes a considerable increase in particle size (15). Evidence has also been obtained for an increase in particle size with increasing pH, as well as with increasing acidity. Carnigiia (15) investigating the adsorption of colloidal Pu (IV) by glass reached the following conclusions:

1. Colloidal Pu (IV) is a positive colloid which is electrostatically adsorbed on substances such as paper, cotton, sand and glass, which assume negative surface charges when immersed in water.
2. The susceptibility to adsorption is a function of particle size, larger particles being less adsorbed.
3. Saturation of a glass surface occurs with the adsorption of approximately 1 µg of plutonium (IV) per square centimeter of surface area. The charge to plutonium ratio of the polymer has been estimated to be approximately 0.1.

The plutonium aggregate can be formed from many solutions. Its formation is favored by an increase in the plutonium concentration, an increase in the temperature or a decrease in the acidity. The presence of strong complexing anions inhibits the formation of the polymer. However, the presence of polymeric plutonium or aggregates should be assumed whenever the acid concentration is below 0.5M. If an acid solution of plutonium is diluted with water, polymerization occurs due to the existence of transient regions of high pH, even though the final acidity may be high enough to prevent formation of the polymer.

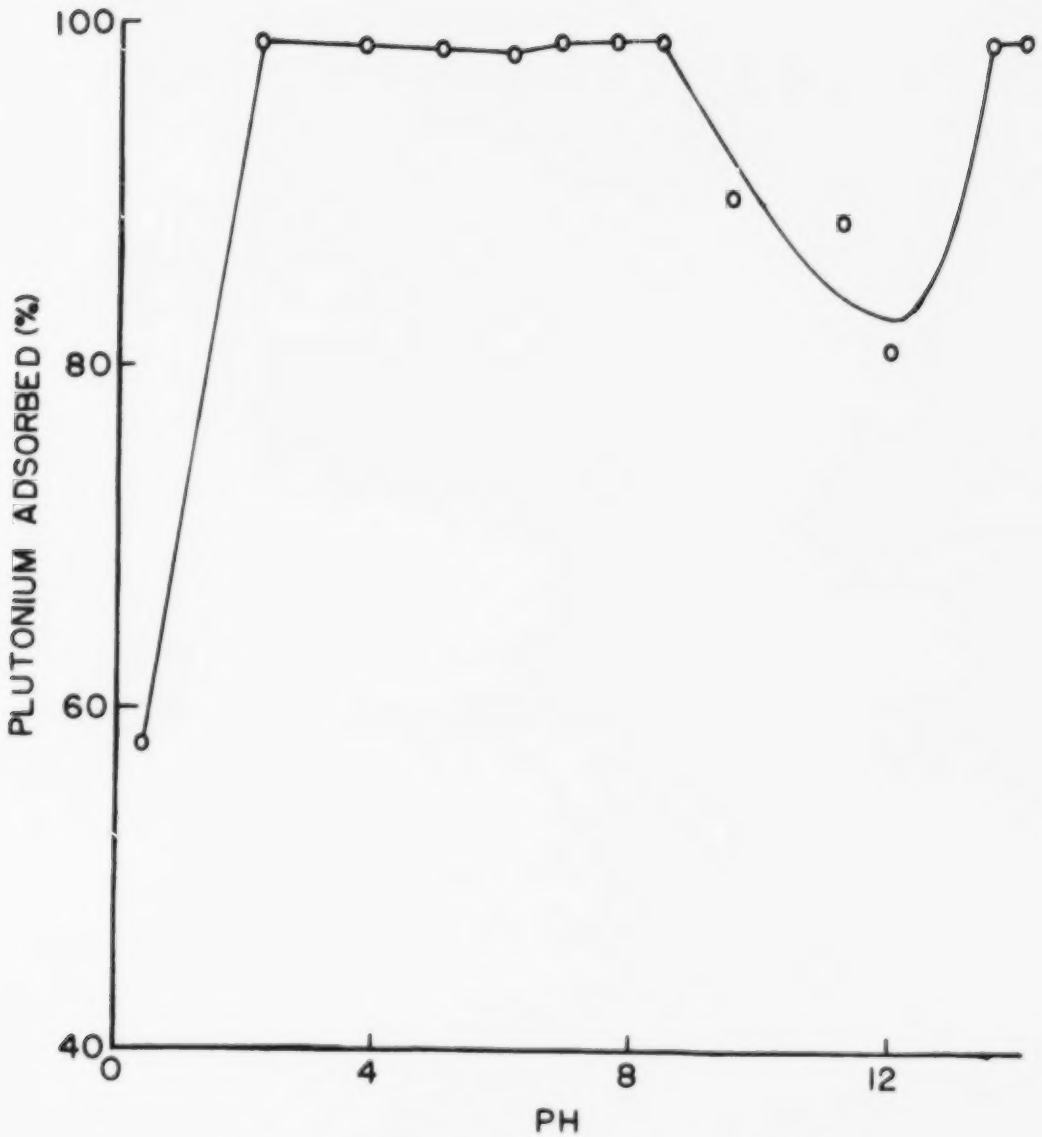
Depolymerization is very slow at room temperature in moderate acid concentrations. The rate is increased by heating, stronger acid concentration,

and addition of strong complexing agents such as fluoride and sulfate (26).

In addition to the work of Carniglia mentioned above, other workers have studied the strong sorption of the Pu (IV) polymer or aggregates on various materials (19, 10, 14, 16, 17, 21, 29). Rhodes (10) noted that when slightly acid and neutral solutions were added to a calcareous soil, more than 90 percent of the plutonium was effectively taken up by the soil. Since in this range of acidity the tetravalent plutonium exists as the hydroxide polymer, further evidence is obtained for the strong affinity of this form for soil. The effect of pH which Rhodes found is shown in Figure 3. Between pH 2 to 8 and above pH 13 plutonium uptake by the soil was virtually complete. However, in the alkaline pH range, 8 to 13, the uptake of plutonium was apparently inhibited.

This experiment by Rhodes involved a solution/soil ratio of 20/1 and HCl or NaOH was used to adjust the pH of the system. The soil was shaken with the plutonium solution for 24 hours. After shaking, the samples were centrifuged and an aliquot of the supernatant liquid was removed to determine the concentration of plutonium and the equilibrium pH. Although Rhodes gives no indication of the centrifugal force to which his samples were subjected, or for how long they were centrifuged, the present research has shown that up to 30 percent of the plutonium polymer is centrifuged out at relatively low speeds with a centrifugal force of about 30 g's for six minutes. It is believed, therefore, that the actual amount of plutonium sorbed in Rhodes work was much less than that reported. How much less is dependent upon the centrifuging speeds and times and the pH of the solution.

In an experiment to determine the uptake by plants of plutonium sorbed on soil colloids, Jacobson and Overstreet (12) also centrifuged a soil-nuclide suspension as a means of determining the extent of sorption. The pH at which

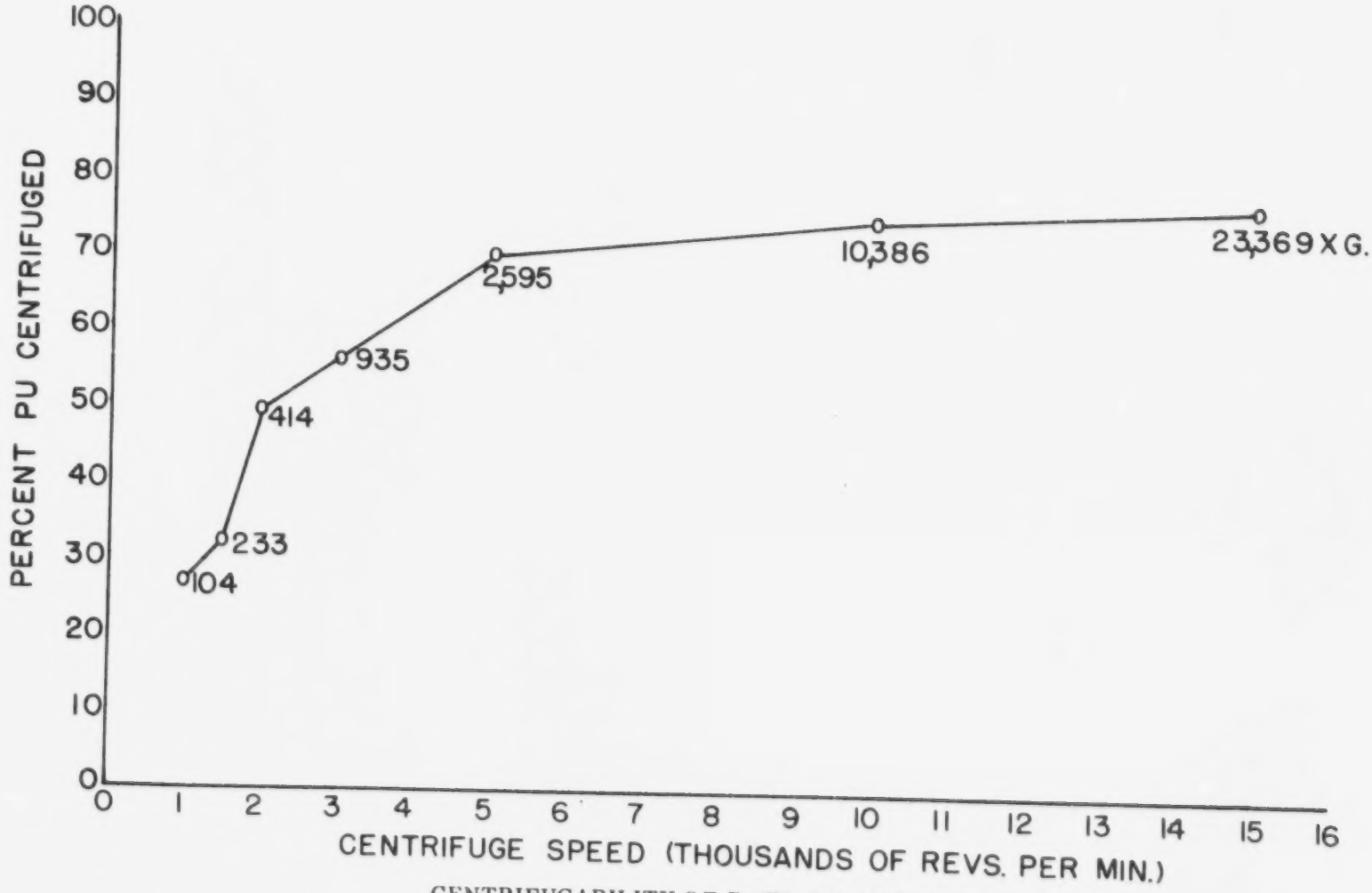


SORPTION OF Pu BY SOIL AS A FUNCTION OF pH
(AFTER RHODES)

FIGURE 3

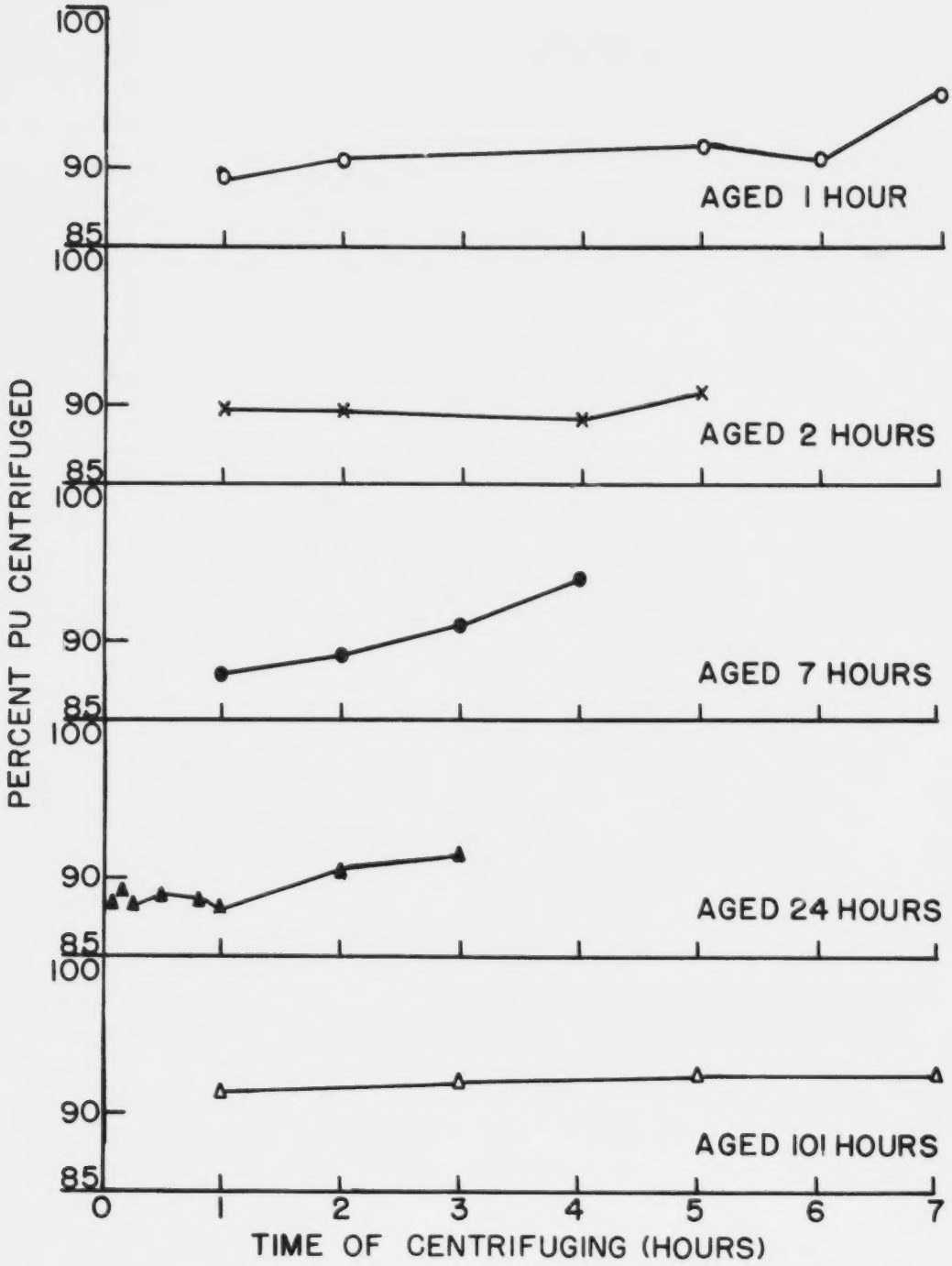
they worked, 5.5, was high enough that the Pu (IV) would have been polymerized and thus possibly centrifuged out of solution. They obtained a value of 66 percent of the Pu (IV) sorbed on the soil, which was calcium bentonite. Here again it is suspected that this reported value may be high.

The above criticisms regarding the sorptivity of Pu (IV) were reached after studying the centrifugability of plutonium aggregates at pH 7 as a function of the speed of centrifuging. Typical results obtained in this laboratory are shown in Figure 4. In this experiment the concentration of the plutonium was measured before and after centrifuging by alpha counting a small aliquot of the supernatant liquid. In another study the centrifugability of plutonium at pH 6.8 was determined as a function of time of aging of the aggregates and time of centrifuging. These solutions were centrifuged at 19,000 rpm (31,500 g's) for times up to seven hours after being allowed to age for periods up to 10^{7} hours. These results are shown in Figure 5. Only small differences were found in the centrifugability at this high speed due to aging, although Ockenden and Welch (18) observed spectrophotometric differences in fresh and aged polymer solutions which indicates a possible change in the character of the polymer. Differences were observed in this laboratory when solutions of different ages were centrifuged at a lower speed. For example, a solution was prepared by adding concentrated HNO_3 to a 2.6 M HNO_3 solution (10^{-6}M Pu), diluting with water and titrating to pH 7 with NaOH, after which pH 7 phosphate buffer was added to bring the final volume to 100 ml. In this solution 8, 13 and 16 percent of the plutonium centrifuged out after aging for 1, 2.5 and 4 hours, respectively, to allow for growth of the plutonium aggregates. However, a solution prepared in the same manner the next day, and within a tenth of a pH unit, gave 28.5 and 36.8 percent centrifugation after one and four hours, respectively. This property of the



CENTRIFUGABILITY OF Pu(IV) AGGREGATES AT pH 7

FIGURE 4



CENTRIFUGABILITY OF Pu(IV) SOLUTIONS OF DIFFERENT AGES

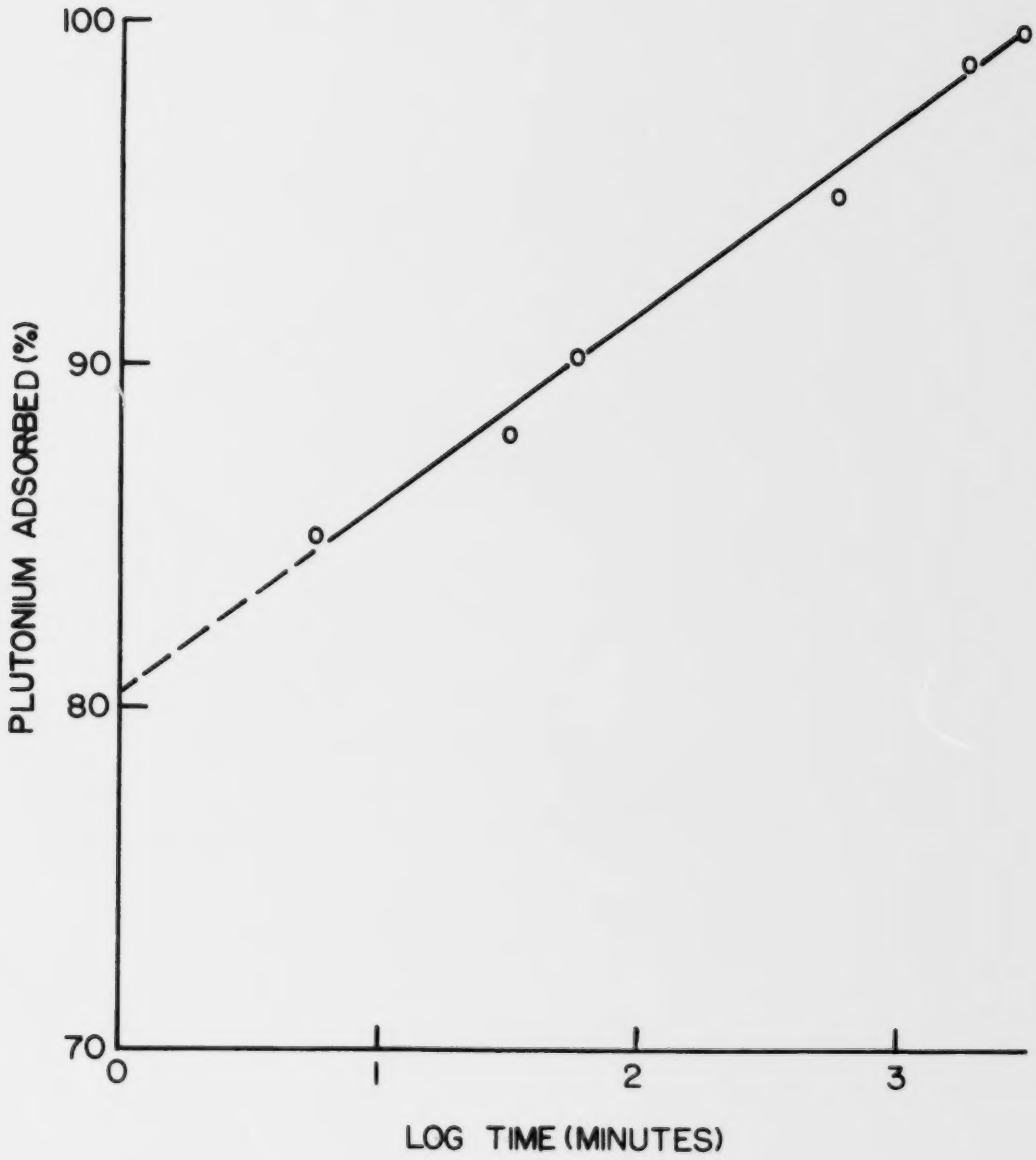
FIGURE 5

plutonium polymer of forming and behaving differently each time it is prepared makes the reproducibility of experiments extremely difficult. The relative irreproducibility for a fresh solution is much greater than for an aged, and thus more stable, solution. Since the age of the polymer is important in determining its sorption behavior, care must be taken to accurately describe the solution used in any experiment. All solutions, fresh as well as aged, are likely to have very small amounts of plutonium in oxidation states other than (IV) as disproportionation is always occurring, if only at a slow rate.

Further evidence that the plutonium is centrifuged out of solution was actually obtained by Rhodes, but was not applied in his analyses. An ultrafiltration technique (30) was used which showed that at pH 8.2 the ratio of ionic to polymeric Pu (IV) is 0.05. In other words, at this pH approximately 95 percent of the plutonium is non-ionic, and large enough to be filtered by a dialyzing membrane. More recently, Lindenbaum and Westfall (20) used an ultrafiltration technique and a similar membrane to obtain a value of approximately 90 percent of the Pu (IV) being non-filterable at this pH. It is this non-filterable Pu (IV) polymer which is centrifuged out of solution.

Rhodes also studied the sorption of plutonium on the soil as a function of contact time and obtained the curve shown in Figure 6. The extrapolation which Rhodes has made tends to indicate that 80 percent sorption can occur in one minute. Such a fast rate is very difficult to imagine for this type of sorption system. Here again the experimental techniques used led to reported values of plutonium sorbed which are probably unrealistically high.

That the plutonium polymer is so centrifugable is due to the polymeric aggregates mentioned above. The molecular weight of the polymer has been estimated at around 2×10^5 (20). Okenden and Welch (op cit) found that the minimum molecular weight of polymeric Pu (IV) is about 4×10^3. It has been noticed in the present research that, in bulk solutions (100 to 200 ml) of Pu (IV), appreciable settling takes place when the solution is allowed to stand.



SORPTION OF Pu(IV) BY SOIL AS A FUNCTION OF TIME
(AFTER RHODES)

FIGURE 6

B. Sorption of Plutonium onto Silica

1. Method of Analysis

A "direct" method for determining the amount of plutonium sorbed on the mineral has been developed and tested in this laboratory. With this method the mineral, after sorbing the isotope, is separated from the supernatant liquid by filtering it with a No. 1 Whatman filter, slight vacuum being used. The mineral is then washed with buffer of the same pH as the plutonium solution and dried under a heat lamp. After drying all or part of the mineral is transferred to a small tared beaker and weighed. One milliliter of concentrated HNO_3 is then added to the beaker to leach the plutonium from the mineral. Aliquots of the leaching acid are taken for counting. From the known weight of mineral in the beaker, the amount of plutonium sorbed per gram of material is determined.

This "direct" method has distinct advantages over the "difference" method in which the amount of plutonium sorbed is determined by the difference in concentration of the supernatant liquid before and after the contact period. First, as pointed out earlier, centrifuging the mineral out of solution also removes a large amount of unsorbed plutonium. In addition the "difference" method can not conveniently account for the plutonium which may sorb on the sides of the reaction vessel. This does not present a problem with the "direct" method.

The plutonium solutions are generally prepared in a manner designed to assure that the Pu (IV) oxidation state will predominate, and to obtain a final concentration of approximately 10^{-7} M. To a volume of the "working" solution (10^{-6} M Pu in approximately 3 N HNO_3) is added concentrated HNO_3. After standing for five to ten minutes

the solution is diluted by adding filtered, double distilled, demineralized water dropwise. Sodium hydroxide is then added slowly to titrate the solution to the desired pH. Buffer of this pH is then added to give the final volume.

After addition of the buffer the solution is ready for contact with the mineral if a fresh solution is being studied. If it is desired to age the solution to allow the polymer to grow, it is stirred continuously with a magnetic stirrer and teflon bar. The growth of the polymer in this, as well as the solutions in contact with the mineral, is followed by filtration through filters of known pore diameters.

The plutonium is determined by alpha counting in an internal proportional counter. A small volume is evaporated on a stainless steel planchet. The planchet is then flamed over a burner and placed in an oven at 140°C overnight and counted.

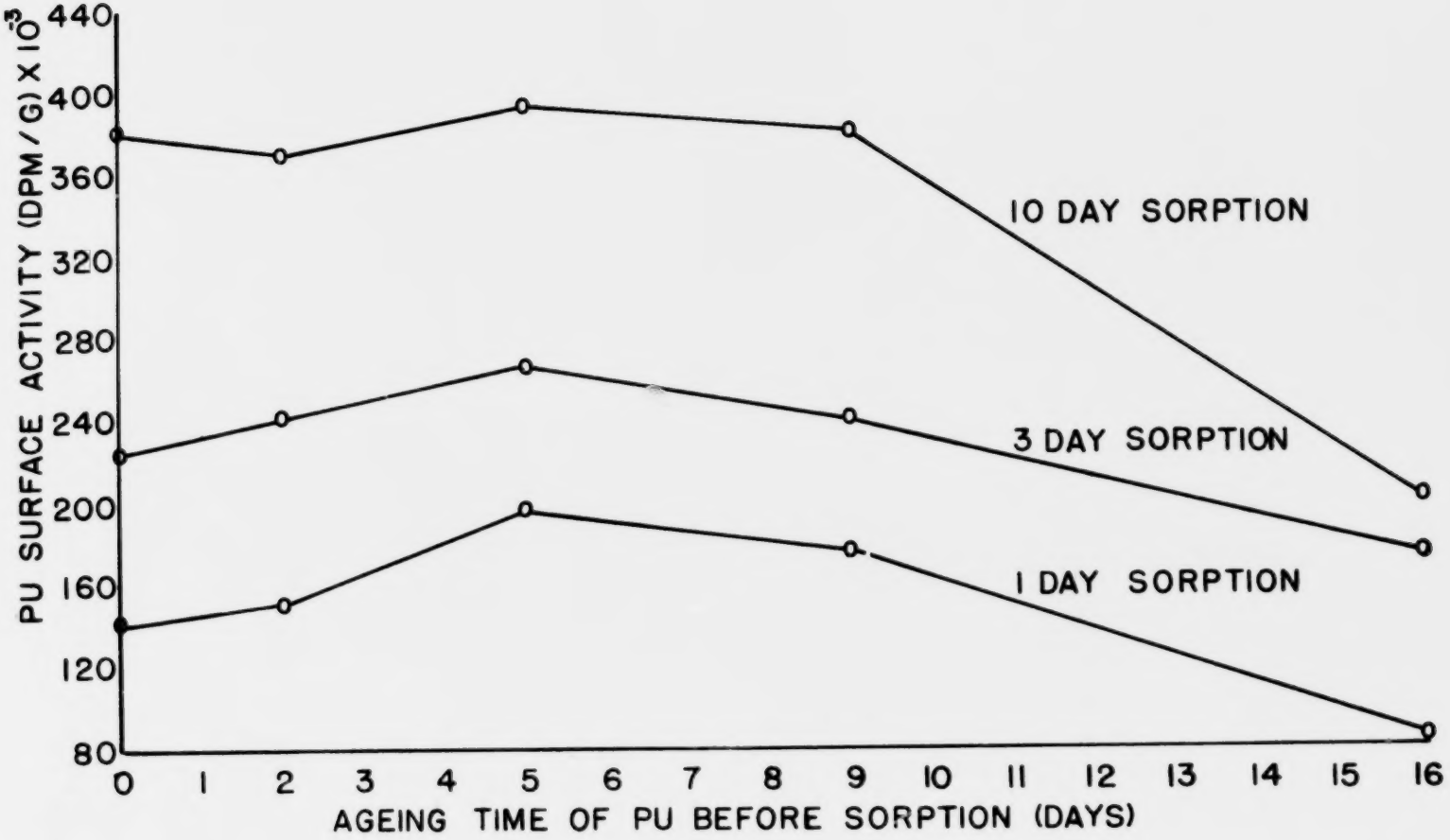
2. Sorption as a Function of Age of the Plutonium Solution

The plutonium aggregates have been found to vary in size with age, becoming larger with stirring and age. Evidence also points to the fact that the large (filterable) aggregates are sorbed in preferance to the smaller material. To test this further the effect of aging of the plutonium solution was studied in relation to its sorption onto silica. A large master solution of pH 7 Pu (IV) (10^{-7} M) was prepared and, at times ranging from zero to sixteen days, aliquots were taken to which silica was added for sorption. While aging, the master solution was stirred with a magnetic stirrer at room temperature. The silica used was Ottawa "Bond", which is a coarse silica. The total plutonium

sorbed per gram of silica (in DPM/g) is given in Figure 7 for one, three, and ten days of contact for the solutions which had aged for the times shown (i.e., 0, 2, 5, 9 and 16 days) before the silica was introduced and sorption begun. It appears that sorption increases with age of the solution up to five days and decreases thereafter. Thus, in aging, the aggregates attain an optimum size or other characteristic which renders them more sorbable. It is quite probable that at this point the size to charge ratio is at its maximum value, thus increasing the electrostatic attraction between the plutonium aggregates and the silica surface. In summary, although the sorption of all solutions increased with time, the age of the solution and, therefore, the state of the plutonium greatly influences the rate of sorption. All the solutions studied showed an increase of sorption with time.

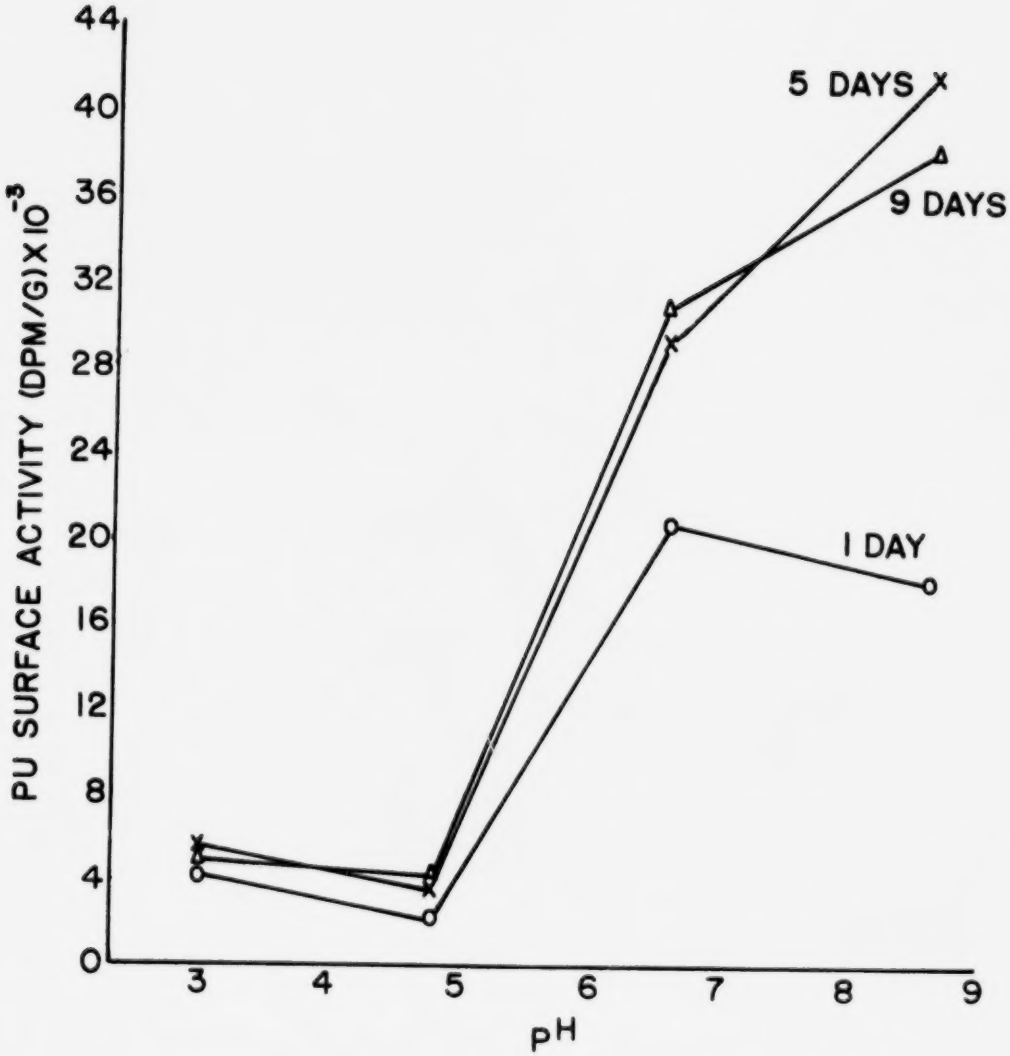
3. Sorption as a Function of pH

Four 10^{-7} M Pu (IV) solutions were prepared at a pH of 2.9, 4.7, 6.6, and 8.7, respectively. These solutions were then shaken with "Bond" silica at a volume to mass ratio of 20:1. Samples taken at one, five, and nine days gave the results shown in Figure 8. There is greater sorption at pH 3 than at 4.7, probably due to the presence of some ionic Pu (IV). At pH 4.7 the Pu (IV) undergoes hydrolysis and polymerization, but the polymers probably remain relatively small, do not tend to aggregate and have a low size to charge ratio. Above this pH there is rapid increase in the size of the polymer and its aggregates,



SORPTION OF Pu(IV) AS A FUNCTION OF AGE OF THE SOLUTION

FIGURE 7



EFFECT OF pH ON THE SORPTION OF Pu(IV)

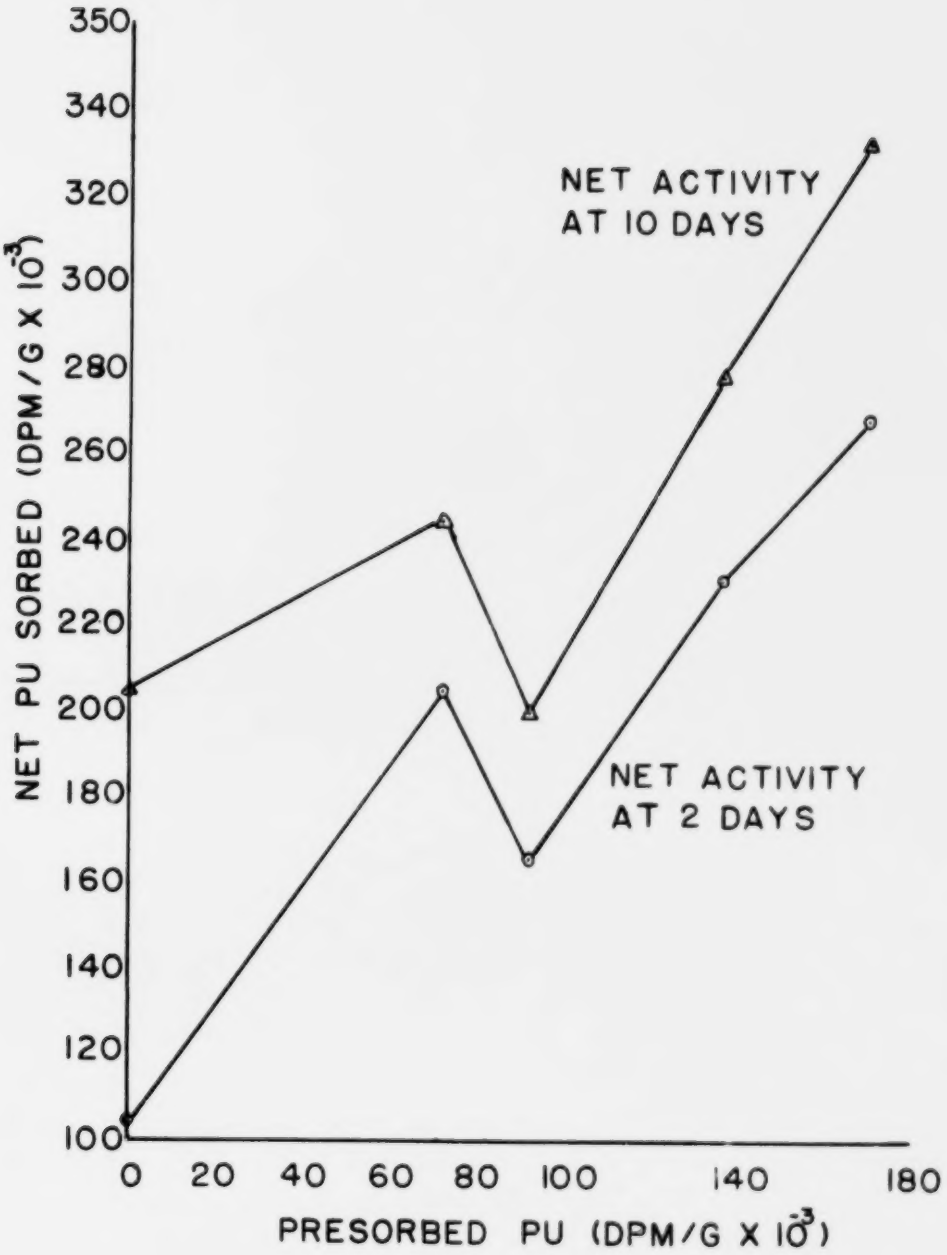
FIGURE 8

as well as precipitation of $Pu(OH)_4$, and a more sorbable species emerges with a more favorable size to charge ratio. The more favorable species for sorption may form faster initially in the range of pH 7 than at pH 9, accounting for the decrease in sorption at one day. The aggregates continue to grow, and at five and nine days give higher values. No significance is attributed to the fact that the five-day value for pH 8.7 is higher than the nine-day value.

4. Sorption as a Function of the Amount of Plutonium Presorbed

Since plutonium aggregates are presumed to form and grow by the collision of basic polymer units and small aggregates, it seemed plausible that growth of the aggregates would occur on the surface of the silica, as well as in the bulk solution. If growth of the aggregates occurs on the silica surface, and if such growth is as fast or faster than sorption on a bare surface, then a silica surface partially covered with plutonium aggregates should sorb additional plutonium at a higher rate than one with no initial plutonium. It also follows that there should be an increase in sorption with increasing amounts of plutonium presorbed.

To test this hypothesis several flasks were prepared with varying plutonium surface activities on Bond silica. The silica was then introduced to a new 10^{-7} M pU (IV) solution and sorption allowed to proceed as usual. Samples were taken at two and ten days, and the net plutonium sorbed for these periods was determined as a function of the initial surface activity. The results are shown in Figure 9. It is apparent that the amount of presorbed plutonium significantly increases subsequent sorption, particularly for short sorption times or large amounts of presorbed plutonium.



EFFECT OF PRESORBED Pu(IV) ON SUBSEQUENT SORPTION

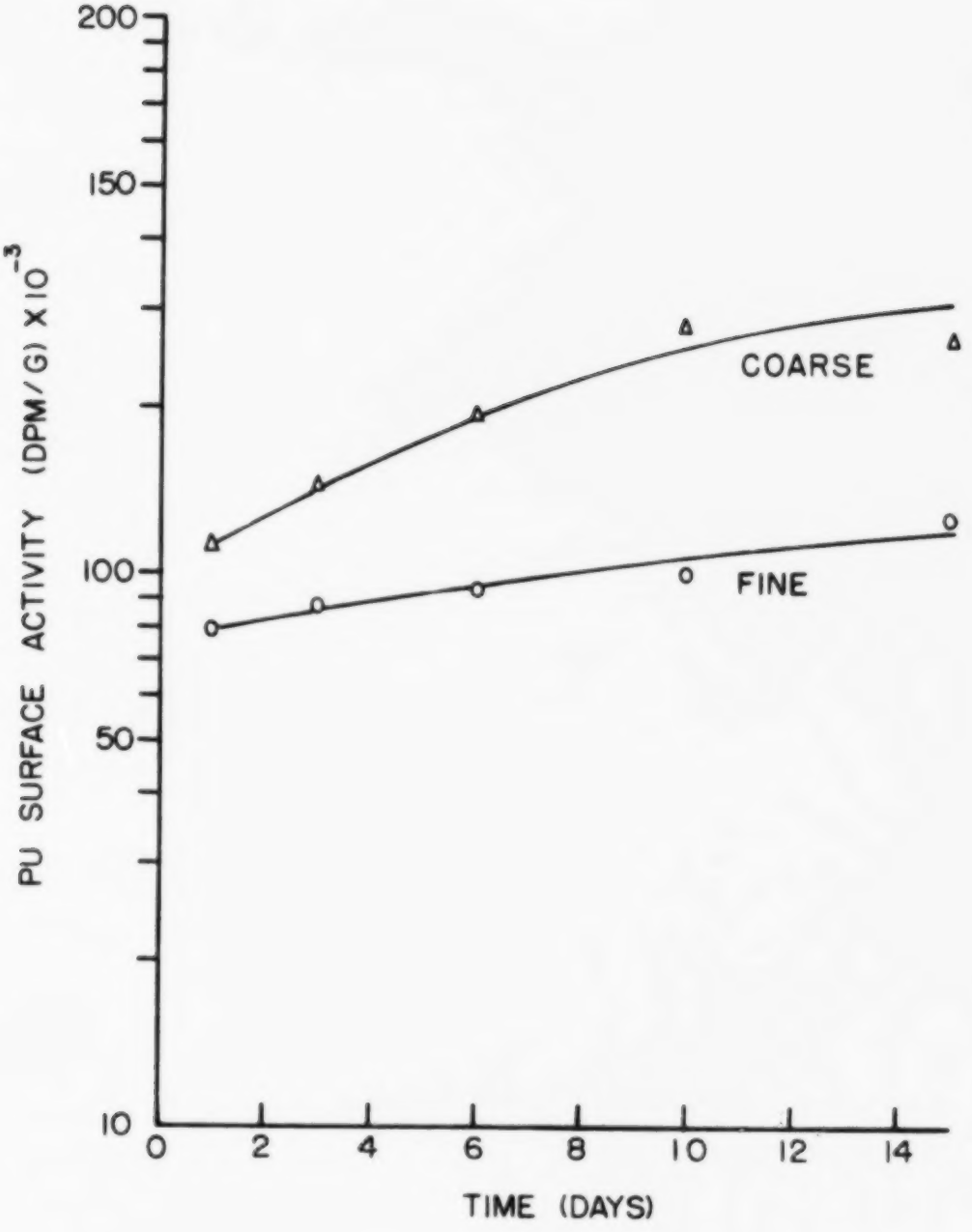
FIGURE 9

One can hypothesize two reasonable mechanisms for this effect. There could be a greater affinity between plutonium aggregates than between an aggregate and an uncovered silica surface. On the other hand it is possible that there is little or no difference in these affinities; rather the presorbed plutonium simply acts to increase the total surface area, providing more sites for sorption. In fact the attachment of a plutonium aggregate to a previously sorbed aggregate may not be the same type of sorption that occurs between plutonium and silica; but when viewed macroscopically the two are indistinguishable.

5. Sorption as a Function of Silica Particle Size

As the particle size of the mineral is decreased, the surface area per unit weight increases inversely in proportion to the diameter. Generally it is expected that as a first approximation, sorption will be in direct proportion to the surface area available. However, there is the possibility of specific mineral particle size effects other than that associated with the amount of surface area. For example, because the silica particle is charged, the charge per weight will vary with particle size and could affect the sorption of plutonium.

Using a fine silica with a mean diameter of 150 microns and a coarse silica of approximately 500 microns mean diameter, the sorption of Pu (IV) was studied. Initially, it was found that the extent of sorption was the reverse of that expected purely on a surface area basis. Figure 10 shows the results obtained when equal weights of the two silicas were contacted with a 10^{-7} M aged Pu (IV) solution.



EFFECT OF SILICA PARTICLE SIZE ON Pu(IV) SORPTION

FIGURE 10

The 150 micron silica has a calculated surface area of 1.5×10^{-2} m^2/g while the surface area of the coarse silica is 4.5×10^{-3} m^2/g. However, in spite of the fact that the fine silica has approximately 3 times the surface area per gram of the coarse silica, the latter sorbs 2.7 times as much Pu (IV) per gram in ten days and 2.2 times as much in 15 days. The area per particle for the fine and coarse silica is 0.706×10^{-3} cm^2 and 7.85×10^{-3} cm^2, respectively. Thus a coarse particle has 11.1 times the surface area of a fine particle; yet the Pu (IV) activities per particle have been calculated as 47.4 and 0.47 DPM/particle for the coarse and fine silica, respectively, a ratio of 100:1.

It has already been shown that the Pu (IV) polymer aggregates which are preferentially sorbed are large and somewhere in the range 50 to 100 microns. It is easy to visualize that there might be a geometric or steric problem when these large Pu (IV) particles attempt to sorb onto silica particles of nearly the same size. The size of the fine silica may limit the amount of plutonium growth which can occur on the silica surface. It is also possible that the smaller size silica sorbs only smaller size Pu (IV) particles. If, for instance, the size of the Pu (IV) sorbed is in proportion to the size of the silica, the factor of 100 in the activity per particle relationship is accounted for. In other words, if the large silica particles, which have an area approximately ten times as great as the fine particles, sorb Pu (IV) aggregates which are approximately ten times those sorbed by the fine silica, then the ratio of activity per particle would be approximately 100:1, the ratio obtained experimentally.

6. Sorption as a Function of Temperature During Hydrolysis

If the size of the Pu (IV) aggregates which form following hydrolysis and the formation of the hydroxide are affected by the temperature of the solution upon the addition of base, the subsequent sorption might likewise be affected. To determine if there is a dependence of aggregate size on the temperature of formation, three solutions were prepared with temperatures held at 4, 20, and 35°C during the addition of NaOH and the raising of the pH to 7. The solutions were then allowed to come to room temperature before introduction of the silica. Sorption was followed over a period of 15 days, as shown in Figure 11.

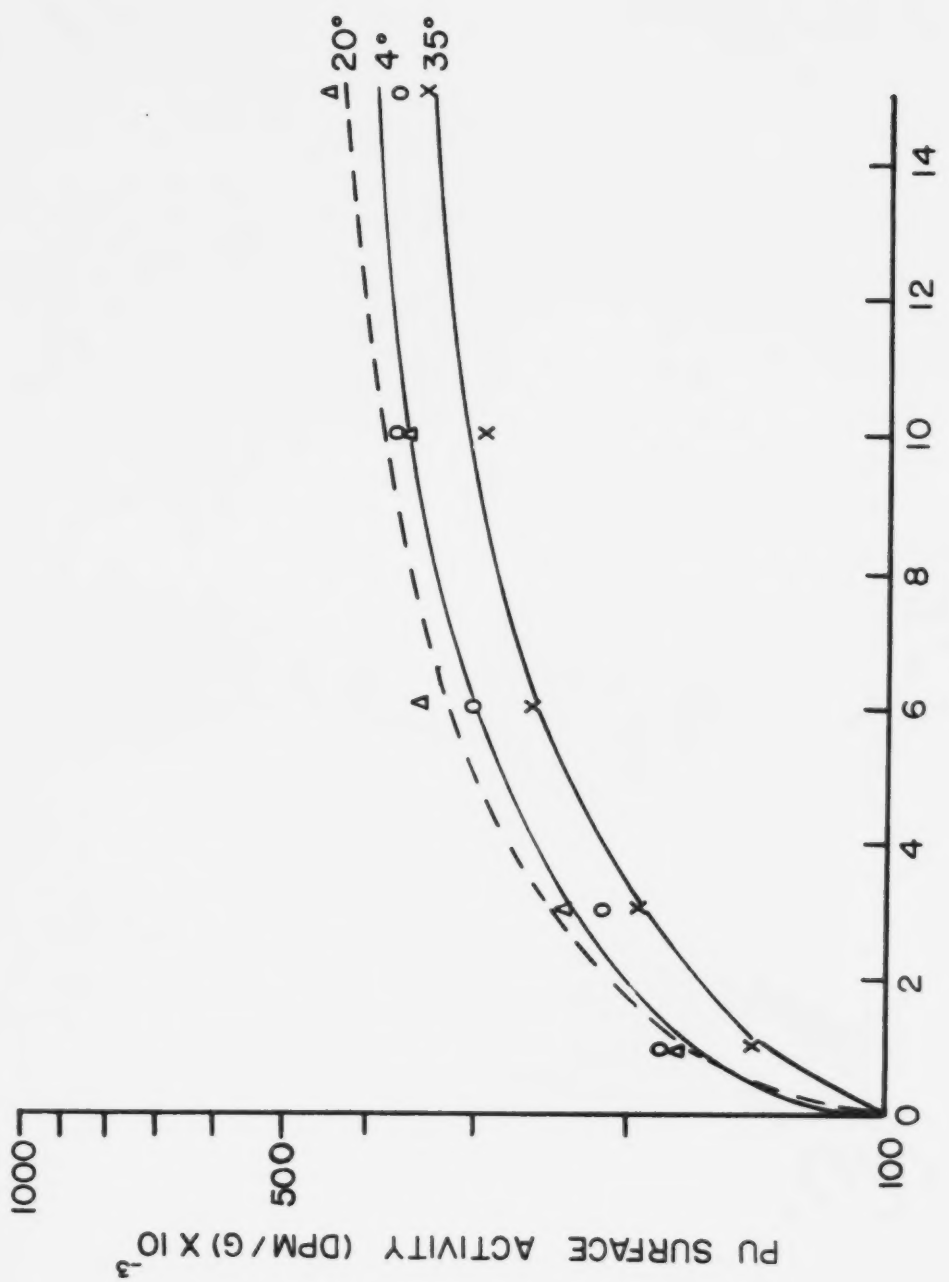
While there appear to be differences in the 4° and 20°C polymers, it is felt that the differences are not significant. Sorption of the 35°C polymer is slightly less than that of the others.

C. Desorption of Plutonium from Silica

The rate of desorption of plutonium from silica and other minerals is very important in predicting the ultimate fate of the radioisotope in rivers and streams. It is also important in the determination of the radioactivity "budget" of a receiving stream, and in setting limits of release of this material into the stream. A study was made to determine the rate and character of desorption and the extent to which it is affected by pH and the age of the sorbed plutonium.

1. Desorption in a Limited Volume Solution

Plutonium was sorbed onto Bond silica for a period of two days at pH 7, after which the silica was removed and rinsed with pH 7 phosphate buffer. Four grams of this silica were then put into 80 ml of the same



EFFECT OF TEMPERATURE DURING HYDROLYSIS ON SORPTION

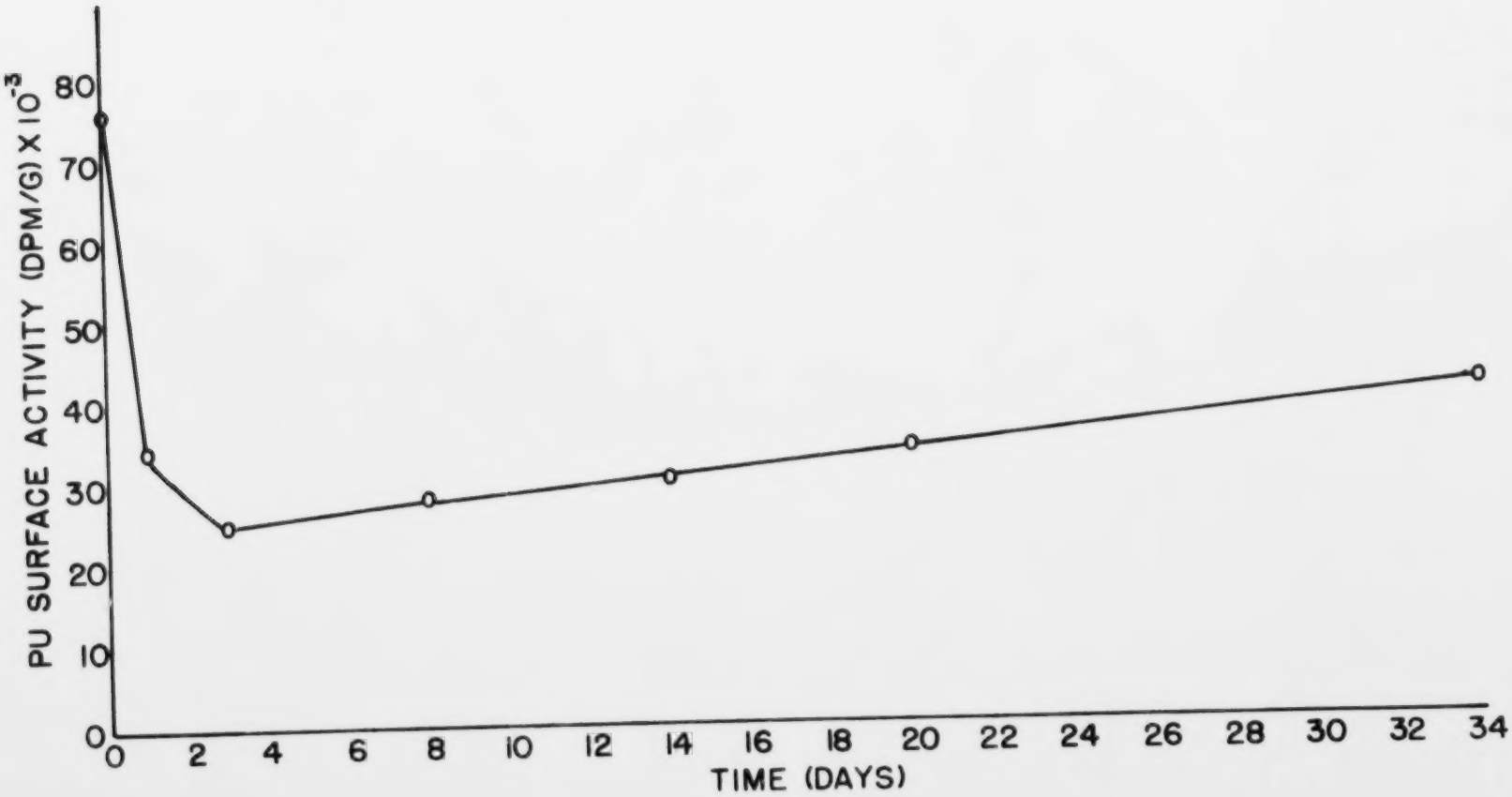
FIGURE 11

buffer and shaken. Desorption of the Pu (IV) was followed over a period of 34 days as shown in Figure 12. The desorption was determined in the same manner as the sorption, i.e., by direct analysis of the plutonium on an aliquot of the silica.

Desorption was rapid during the first day or two and reached a maximum at about three days. It was expected that the rate of Pu (IV) desorption would tend to level off after a few days, but that the Pu (IV) activity on the silica would continue to decrease slowly with time, since the solution volume was large enough to prevent a significant buildup of the plutonium concentration in the solution. However, as shown in Figure 12, the rate of desorption became negative and the Pu (IV) began to resorb onto the silica. It is believed that the plutonium which was initially desorbed consisted of aggregates of less than the optimum sorption size and was thus loosely held at the silica surface or to other plutonium on the silica surface. Once in solution these small aggregates grew in size as they collided with one another and attained the optimum charge to size ratio which permitted them to be resorbed and become firmly bound to the silica surface.

2. Effect of pH on Pu (IV) Desorption

Plutonium was sorbed onto Bond silica at pH 7, then desorbed into an "infinite" volume solution at pH's 5, 7, and 9. The "infinite" volume solution condition was approximated by removing the supernatant liquid at each sampling time and replenishing with fresh solution of the same pH. Thus, there was no significant buildup of the Pu (IV) concentration.



DESORPTION OF Pu(IV) IN A LIMITED VOLUME SOLUTION

FIGURE 12

Figure 13 indicates that there is a significant increase in the rate of Pu (IV) desorption at pH 5. It was previously observed that there was a significantly lower sorption at pH 5 (see Figure 8). Thus, the same phenomena resulting in the lower sorption at this pH are associated with faster desorption. Both the nature of the surface and the plutonium state, as well as their interaction, may be affected by this lower pH.

3. Desorption of Fresh and Aged Plutonium

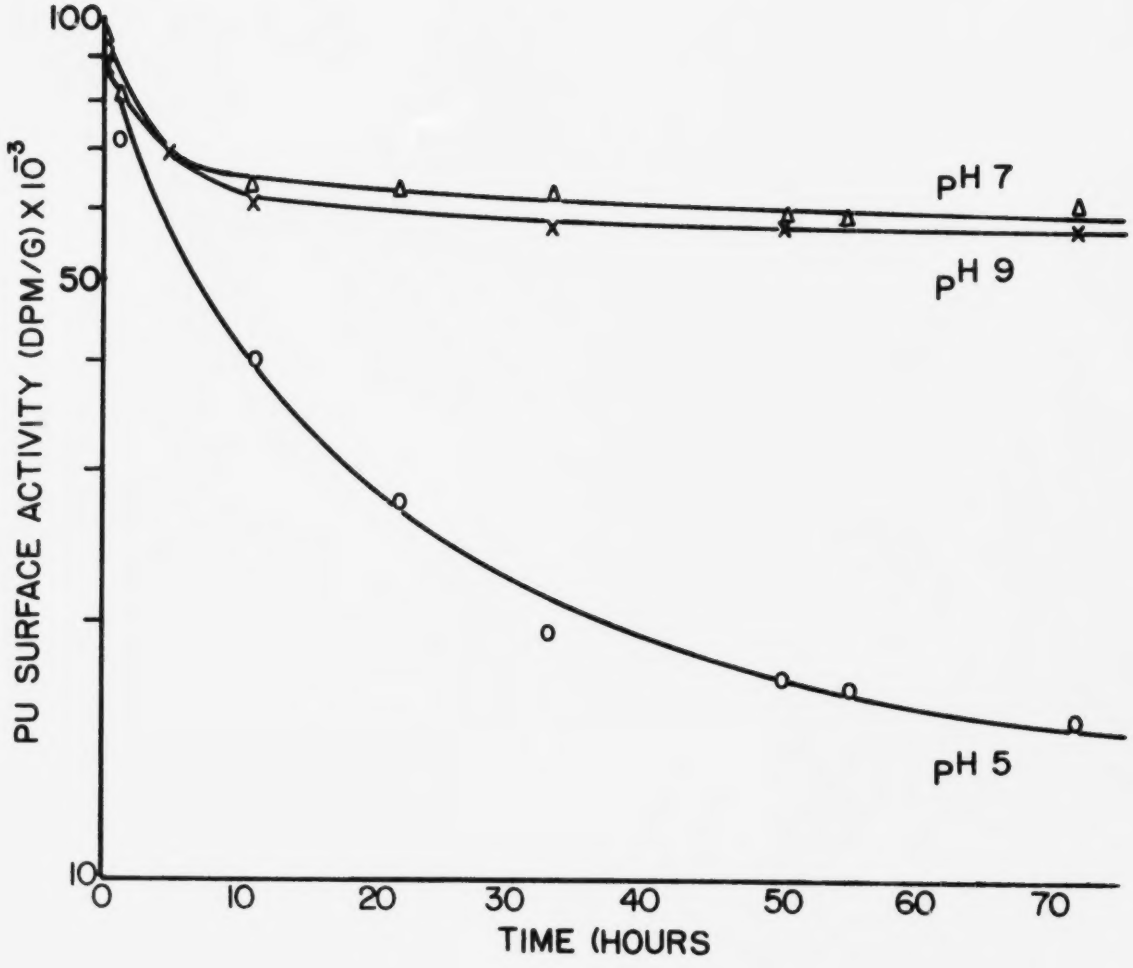
Pu (IV) solutions of different ages sorbed at different rates as indicated in Figure 7. However, the rates of desorption of Pu (IV) which was fresh when sorbed and that which was 34 days old were not very different as shown in Figure 14. The approximately exponential desorption curves may be rather precisely represented as due to two simultaneous first order desorption processes, probably indicating the presence of two different desorbing species. The curves can be divided into two components by extrapolating the nearly horizontal portions (which represent the rate of the 2d component) back to t_o and subtracting these values from the general curve. This gives the curves which represent the rate of desorption of the 1st species. The equation for the 1st component of the curves is then:

$$A_{t(1)} = A_{o(1)}e^{-\delta_1 t}$$

and that of the 2d component:

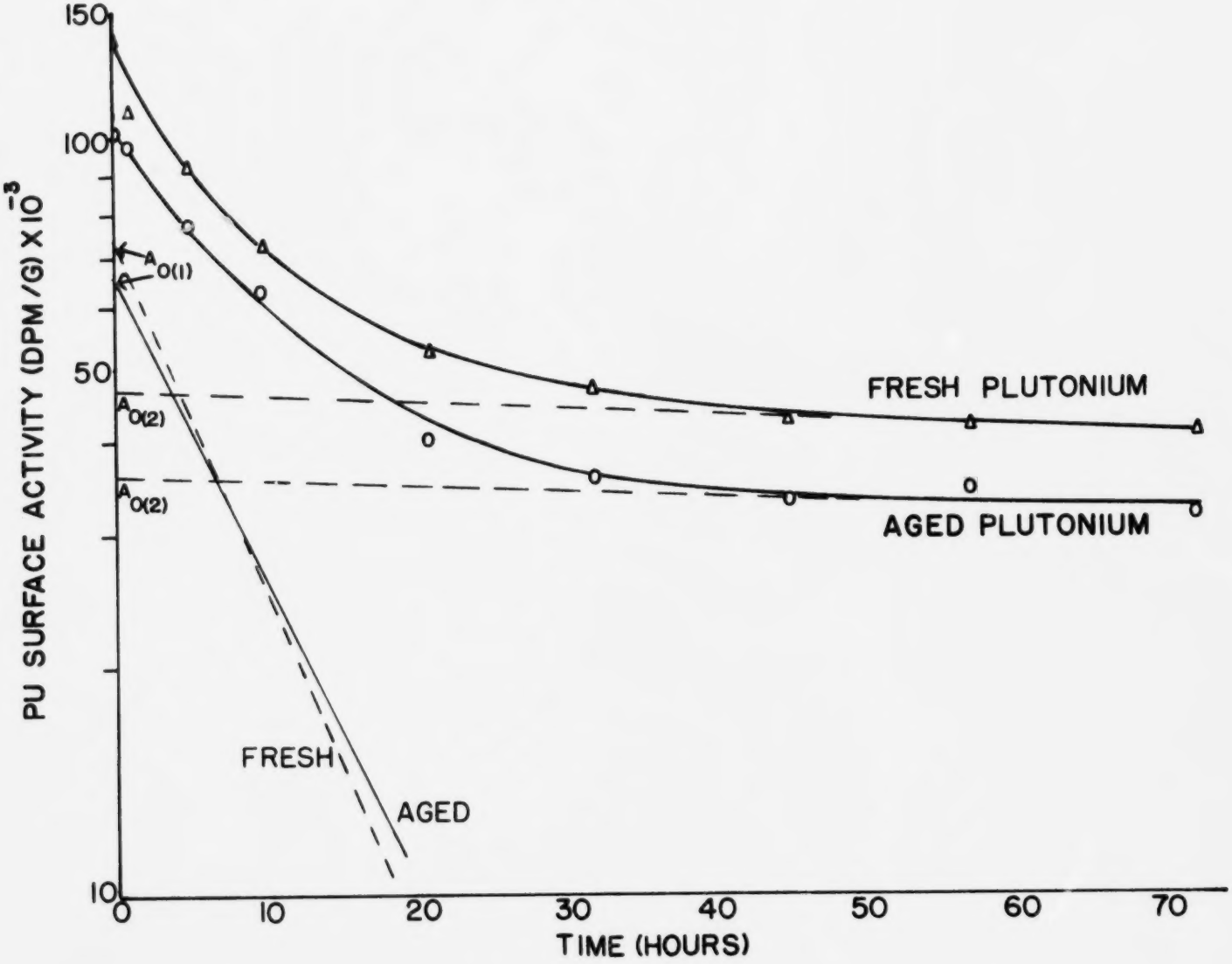
$$A_{t(2)} = A_{o(2)}e^{-\delta_2 t}$$

where: $A_{t(1)}$ and $A_{t(2)}$ are the Pu (IV) activities on the silica surface at time t (in dpm/g).



EFFECT OF pH ON THE RATE OF DESORPTION

FIGURE 13



RATE OF DESORPTION OF FRESH AND AGED Pu(IV)

FIGURE 14

$A_{o(1)}$ and $A_{o(2)}$ are the activities on the silica surface at t_o for species 1 and 2, respectively. δ_1 and δ_2 are the desorption constants for the two species (in hr^{-1}).

The equation for the general curve is then:

$$A_t = A_{o(1)}e^{-\delta_1 t} + A_{o(2)}e^{-\delta_2 t}$$

The values for the desorption constants (δ) are shown in Table I.

TABLE I

Type of Pu (IV) Desorbing	δ_1	δ_2
	(hr^{-1})	
Fresh	0.110	0.002
Aged	0.144	0.002

The small difference in δ_1 for the fresh and agedPu (IV) may be due to the way in which the curves were drawn, to experimental error, or both.

The half-time ($t_{1/2}$) for the 1st species desorbing is readily seen to be between 6.5 and 7.5 hours. While it is not possible to determine $t_{1/2}$ for the second species from the graph, it may be calculated from the relation for a first order decay process

$$t_{1/2} = \frac{0.693}{\delta_2}$$

and is equal to 346 days.

It is the long half-time species which is more likely to be environmentally significant, since it has the ability to remain at its site of sorption for a long period of time and thus remain concentrated. For both the fresh and aged Pu (IV) the ratios of $A_{o(2)}$ to

the initial total activity are 0.337 and 0.346 respectively. Thus, one-third of the sorbed Pu (IV) is strongly held on the silica and desorbs at a very slow rate.

Filtration of the desorbing plutonium with a 15-40 micron porous silica disc indicates that the very first material to desorb is essentially small unfilterable Pu (IV). At the end of the first hour only 2.1 and 3.2 percent of the desorbed plutonium was filterable for the aged and fresh types, respectively. This increased to 17.3 and 15.9 percent at five hours. These results, when compared with those of desorption into a limited volume, lead to the conclusion that the first species which desorb rapidly are small colloidal Pu (IV) particles or ionic plutonium.

D. Characterization and Properties of Silicas

All experiments thus far have been carried out with crystalline silica (quartz) as the sorbing medium. Quartz is the least soluble and most prevalent of the forms of silica (SiO_2) which are stable at ordinary tempera ures. It has a density of 2.65 g/cc.

The structure of a single SiO_2 particle is perhaps best viewed as it appears in an aqueous dispersion. Iler (31) has reviewed the internal and surface molecular structure of silica in such dispersions. Internally there is the classical tetrahedral structure with each silicon atom being surrounded by four oxygen atoms. At the surface the exposed silicon atoms, upon contact with water, may have their tetrahedral bonding completed by a hydroxyl ion, this surface Si-OH species being referred to as silanol.

It is assumed that hydration of silica is confined to its surface and is thus due to completion of surface tetrahedra. It has been shown (31,32, 33)

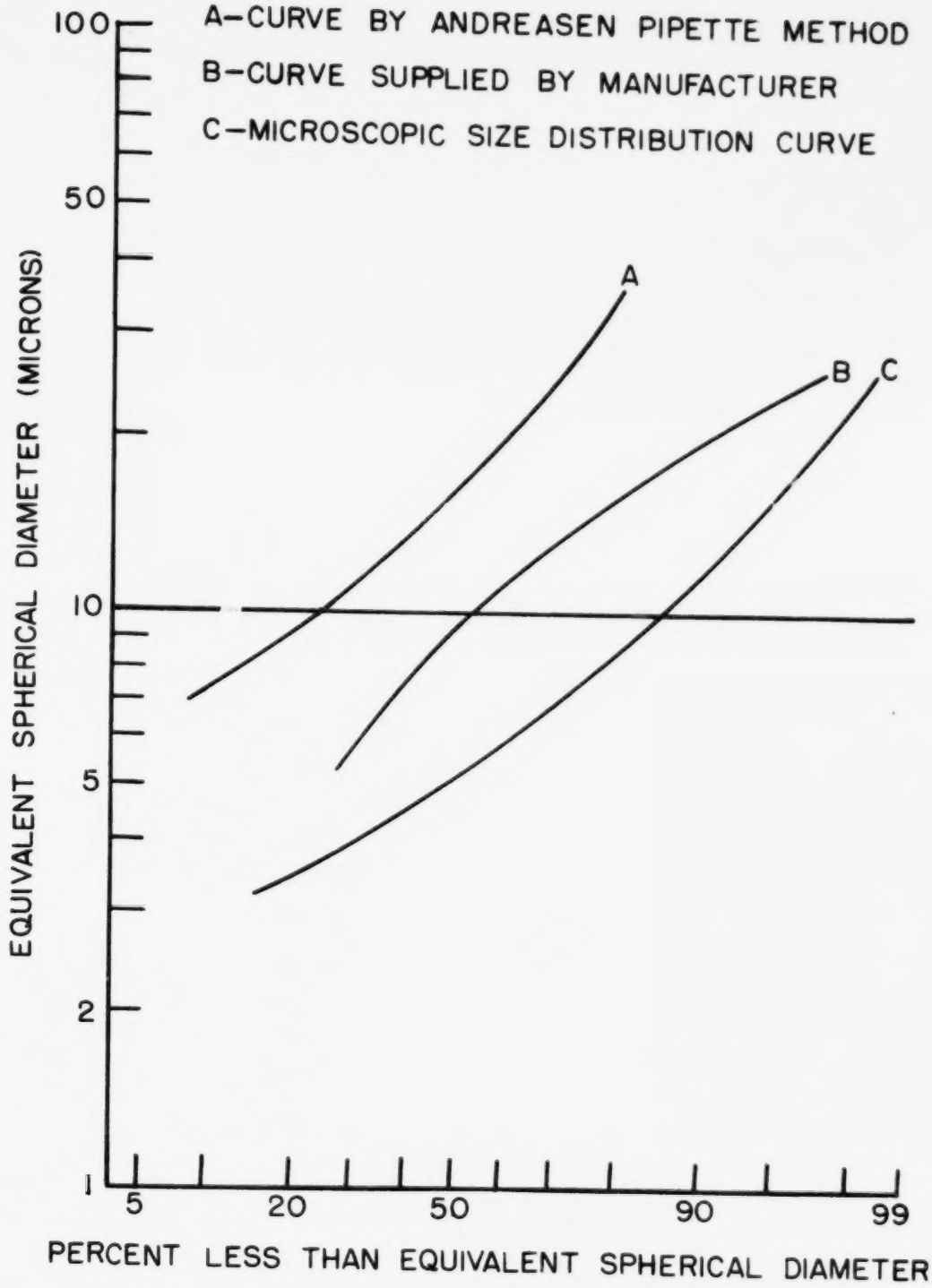
that the silanol group is the site of ion exchange, cations being substituted for the hydrogen ion in the hydroxyl group. Also, the silanol acts as a weak acid, analagous to silicic acid. Thus, the pH of the ambient solution will influence the dissociation of the silanol groups and, hence, the charge on the silica surface.

1. Silica Surface Area and Particle Size

Several different types of silica have been obtained for the sorption work. These range in mean size from 10 millimicrons (QUSO Silica) to 30 microns (Min-u-Sil). Some very large particle size "sands" have also been obtained from the Ottawa Silica Company.

Particle size distributions and surface area measurements have been carried out for several of the silicas. The particle size distributions were determined with an Andreasen pipette. This is a technique based on Stoke's law of settling. It assumes spherical particles and homogeneous density. The size distribution of the 30 micron Min-u-Sil obtained by this method is different from that supplied by the manufacturer. However, it is felt that the data supplied were probably not of recent date and may not have been done with extreme care, since the principal users of this product do not require exact dimensions.

The particle size distribution of the above-mentioned sample was also determined visually with a light microscope. This distribution was different from both the manufacturer's and that obtained by sedimentation. The three curves are shown for comparison in Figure 15. The Ottawa "Bond" silica which has been used in all sorption measurements thus far is a coarse sand. The manufacturer's size distribution is shown in Table II.



MIN-u-SIL PARTICLE SIZE DISTRIBUTIONS

FIGURE 15

TABLE II

MESH	DIAMETER (microns)	% RETAINED	CUM. %
30	600	0	0
40	400	3	3
50	300	35	38
70	200	44	82
100	150	15	97

The surface areas of the nominal 5, 10, 15, and 30 micron Min-u-Sil silicas were determined by titrating the silica with 0.01 N NaOH. Under this method the titer necessary to raise the pH of 1.5 g of silica from 4 to 9 is related to the surface area S (in M^2/g) by the empirical relationship:

$$S = 1.386v - 2.082$$

where v is the titer volume in milliliters. Below is a comparison of the surface areas obtained by the sodium hydroxide titration and those supplied by the manufacturer. It is assumed that the latter were determined by the nitrogen adsorption (BET) method or other similar method. The agreement is quite good.

TABLE III

Sample Designation	Manufacturer's Surface Area (M^2/g)	Area by Titration (M^2/g)
5 micron	2.06	2.51
10 micron	1.10	1.16
15 micron	0.84	0.85
30 micron	0.54	0.52

The ability to determine surface areas was developed early because the extent of plutonium sorption is a function of the surface area.

2. Determination of Silica in an Aqueous Medium

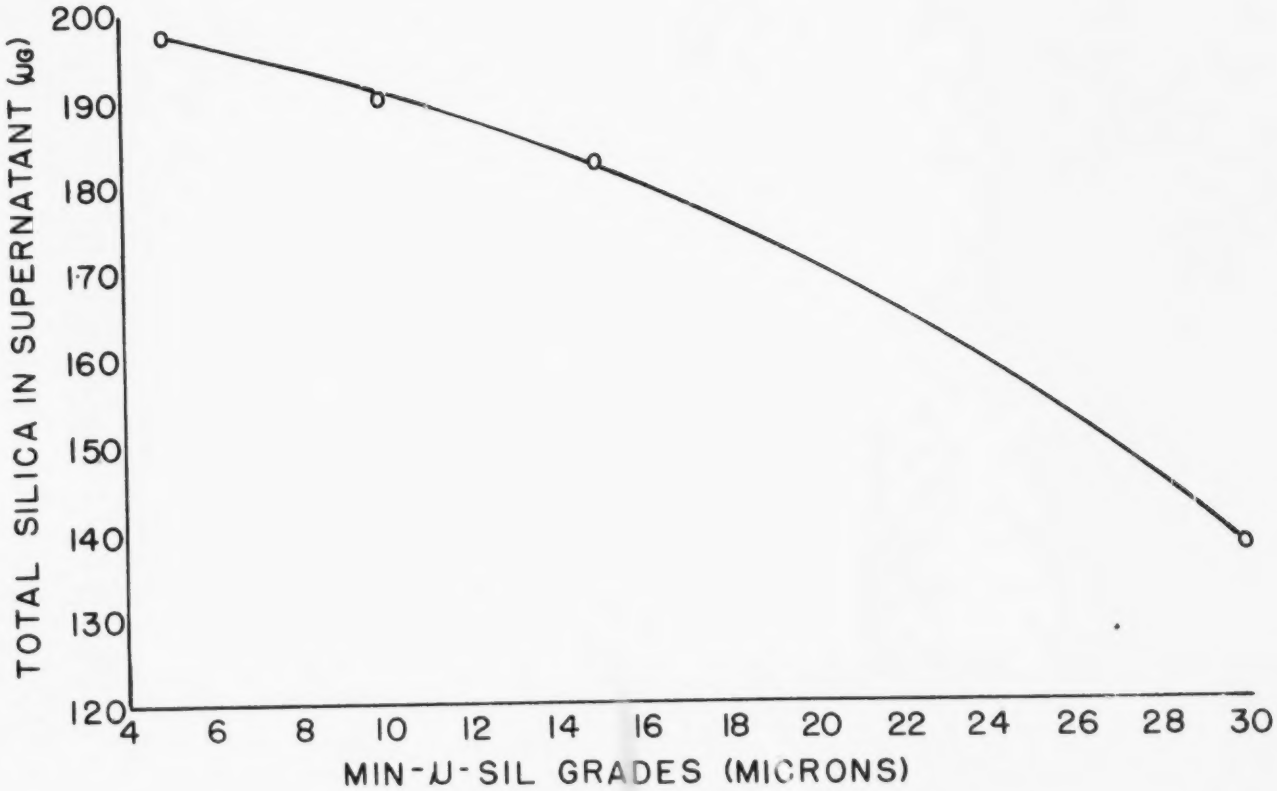
A colorimetric method (34) for determining silica was modified and used to determine soluble and insoluble silica in aqueous solution. With this method, the sensitivity of which allows the measurement of as low as 2×10^{-5}g of silica in 100 ml, it was possible to determine how much soluble and insoluble silica remained suspended following centrifugation.

In studying the extent to which the different silicas are solubilized when shaken with water for several hours and then centrifuged, samples of 0.1 g of each of the Quso and Min-u-Sil silicas were so treated. Two aliquots of the water were then taken and analyzed. To one was added 52% HF in order to determine both soluble and insoluble silica. HF was not added to the second aliquot, the analysis in this case measuring only the soluble silica. In this manner it was possible to distinguish between soluble silica and fine particles remaining in suspension. It was found that after 6-7 hours contact time, only the smallest (10 millimicron) size silica particles gave a measurable amount of soluble silica in the supernatant after centrifugation at 14,000 rpm (20,000 g's) for 15 minutes. In this case, the soluble silica remaining in the supernatant represented 0.19 percent of the total silica added. The other silicas, including one Ottawa sand, had 0.1 to 0.2 percent left in the supernatant following centrifugation,

but this was all insoluble silica, showing up only in those aliquots to which HF had been added. The curve in Figure 16 shows the variation of total (insoluble) silica remaining after centrifugation, as a function of upper particle size for the Min-u-Sil samples.

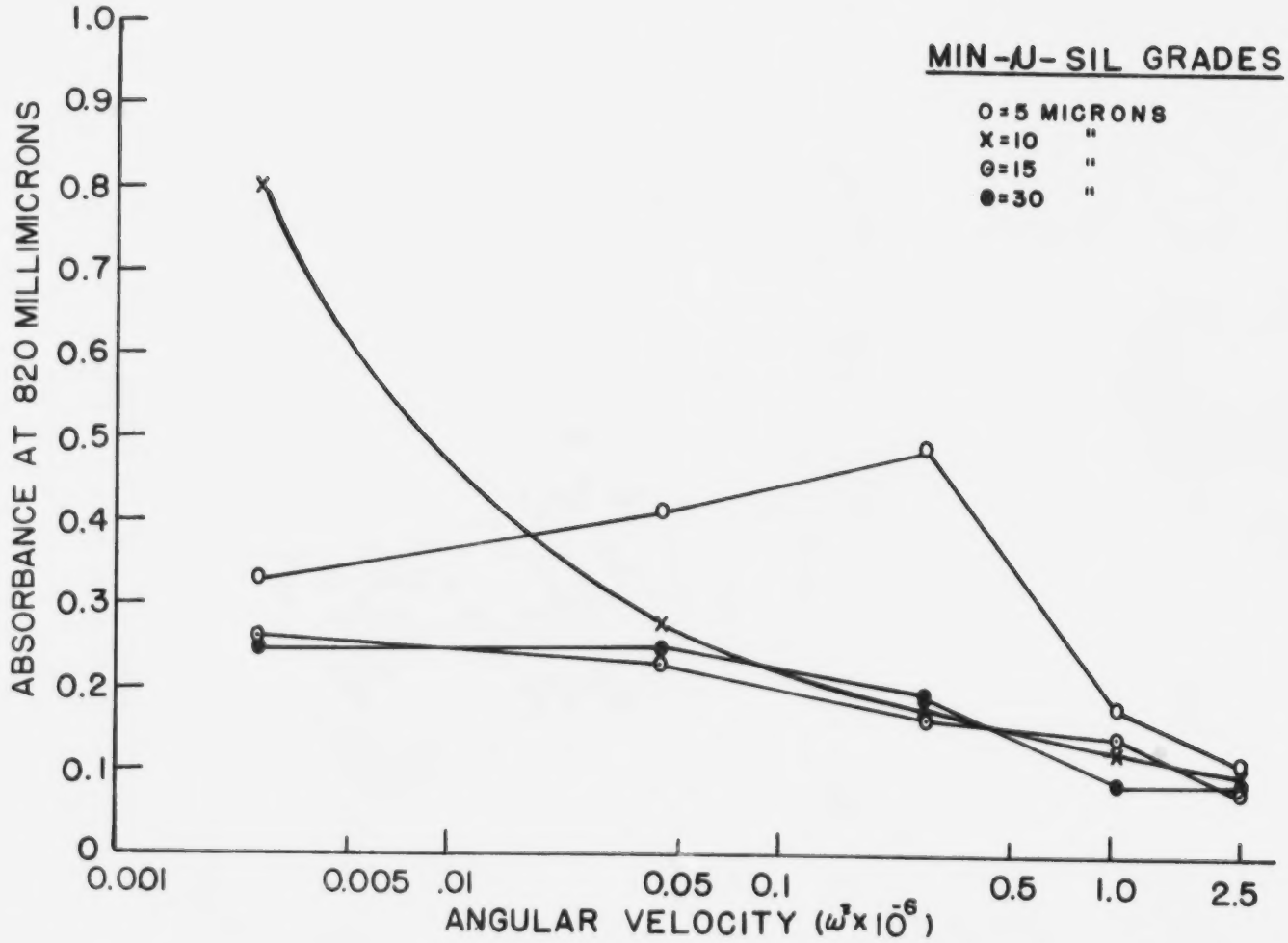
In another study, it was found that for each of the Min-u-Sil samples (except for the 5 micron) there was, as expected, a decrease in the amount of insoluble silica remaining suspended with increasing centrifuge speeds (Figure 17). In the case of the 5 micron material there was a gradual increase up to 5000 rpm, then a drop to the final level of the others at 15,000 rpm.

The silica samples which have been received thus far have been of heterogeneous particle size as indicated above. In order to control the particle size in sorption experiments, several samples have been fractionated into narrow size ranges. This was accomplished by differential sedimentation using Stoke's law of settling. From the 30 micron silica a quantity of very uniform 20-30 micron particles has been obtained. From the 15 micron and 10 micron samples, fractions 10 to 15, and 5 to 10 microns, respectively, have been prepared. The method is slow but efficient. However, there is usually only about 10 to 20 percent of the bulk sample within the given range. Microscopic examination has shown the separated fractions to be exactly as predicted and quite uniform. Below 5 microns attempts are being made to use metal membrane filters because of the inordinately long time of settling of particles in this size range.



NONCENTRIFUGED SILICA Vs SILICA PARTICLE SIZE

FIGURE 16



RELATIONSHIP BETWEEN NONCENTRIFUGED SILICA AND CENTRIFUGE SPEED

FIGURE 17

IV. SUMMARY AND CONCLUSIONS

The most prevalent oxidation state of plutonium likely to be encountered in natural waters is Pu (IV). At pH values above unity, the latter hydrolyzes appreciably to form such species as $Pu(OH)^{+3}$, $Pu(OH)_2^{+2}$ and $Pu(OH)_3^{+}$. Perhaps more important, however, is the formation of $Pu(OH)_4$ which is quite insoluble. The monomeric species of $Pu(OH)_4$ also polymerizes in the pH ranges encountered in natural waters, the monomers being joined by oxygen or hydroxyl bridges. Colloidal and larger size particles of both the $Pu(OH)_4$ precipitate and the polymer aggregates will be encountered in natural waters. Indeed, it is difficult to distinguish between the two and the term "Pu (IV) aggregates" may serve to encompass both species.

Pu (IV) is also known to form complexes with such naturally-occurring anions as sulfate, chloride and nitrate. However, the formation constants of these complexes and the ligand concentrations encountered in natural waters are generally not sufficiently large to form significant amounts of the complex and prevent the formation of Pu (IV) aggregates.

Other oxidation states of plutonium likely to be encountered in aqueous solution include Pu (III), Pu (V), and Pu (VI). Pu (IV) is known to disproportionate into these other oxidation states. However, in natural waters Pu (IV) will predominate.

Both filtration and centrifugation has been used in this research to characterize the plutonium solutions as to the distribution of sizes among the Pu (IV) aggregates and their rate of formation. For example, using filters of varying porosities at pH 7 a Pu (IV) solution aged for four days was shown to contain approximately 90 percent of plutonium aggregates above

one micron in size. This is in contrast to the work of Grebenshchikova and Davydov (19), who found approximately 6 percent less than 1 to 3 mμ and 10 percent less than 30 to 40 mμ. However, Rhodes (10) found at pH 8.2 that 95 percent of the aqueous plutonium is filtered by a dialyzing membrane.

The present research has shown that the mean particle size of Pu (IV) aggregates in the pH range encountered in natural waters is approximately 50 to 100 microns, based on both centrifugation and filtration experiments. Estimates by others of the molecular weight of the polymer are 2×10^5 (20) and a minimum value of 4×10^3 (18). In any event, the present research indicates that the Pu (IV) aggregates are readily centrifuged. For example, in one experiment approximately 30 percent was centrifuged from solution at 100 G's in six minutes. In another, 90 percent was removed at 30,000 G's in six minutes.

The age of the solution greatly influences the size distribution of the Pu (IV) aggregates as shown by filtration through sintered silica discs of varying pore size. This size distribution has a very great effect on the sorption characteristics of the plutonium. In experiments in which the plutonium solution was aged for up to 16 days prior to sorption, such solutions aged for five days gave subsequently higher rates of sorption than solutions aged for shorter or longer times.

It was also found that the sorption per unit surface area was greater onto larger diameter silica particles. Although additional research on the effect of particle size is required, this would seem to indicate that most of the sorbing plutonium would be associated with heavier silica particles which could settle out, rather than being carried along in a stream.

The sorption process onto silica was studied over the pH range of 3 to 9. The rate of sorption is generally slow, even with agitation of the suspension. For example, at a pH of approximately 7 the rate of sorption had not leveled off until five to nine days. A possible rate limiting step in the sorption process is diffusion across the unstirred liquid film (Nernst diffusion film) at the mineral-solution interface. The thickness of this film is primarily controlled by the rate of agitation of the liquid and is generally in the range of 0.01 to 0.001 cm. Usually there is a practical limit below which the thickness may not be reduced (35). For the large plutonium species encountered here, the relatively slow sorption process could be controlled by diffusion across this liquid film.

Since the age of the plutonium solution affects both the Pu (IV) aggregates size distribution, as well as the rate of sorption, this is evidence of the likely effect of aggregate size on rate of sorption, an additional correlation with diffusion as a rate limiting mechanism. However, another possible mechanism of sorption is polymerization or aggregate growth of plutonium already sorbed onto silica. Evidence for this mechanism is the general increase of the rate and amount of plutonium sorption with increasing amount of pre-sorbed material.

The pH of the ambient plutonium solution, both prior to and during the sorption process, is important in relation to both the rate and the amount of sorption. The rate and amount of sorption in the pH range of 7 to 9 is considerably higher than that in the range of 3 to 5. The charge and extent of ionization of the silica surface, the size and charge of the Pu (IV) aggregates, and the equilibria distribution among plutonium oxidation states are all affected by pH and are factors in the sorption process.

The pH of the solution is also important in determining the rate of desorption. The rate into a slightly acid (pH 5) solution is considerably greater than into a neutral of slightly basic solution. The rate of desorption of Pu (IV) from silica is quite rapid at first as the loosely sorbed material comes off. It then decreases to 0.2 percent per hour as the more strongly-bound material desorbs. The tightly-held Pu (IV) desorbs with a half-time of 346 days and constitutes approximately one-third of the sorbed plutonium. If the solution surrounding the silica is not replenished and the initially desorbing Pu (IV) concentration is allowed to build up, there will be resorption as the polymeric aggregates in solution grow to optimum size for sorption.

V. FUTURE WORK

One important area in the continuation of this research concerns the nature of the Pu (IV) aggregate which sorbs onto the various sizes of silica and a better understanding of the effect concerning increased sorption on the large particles of silica. It is hoped that by using a mixture of silica sizes and by desorbing and filtering the polymer, more insight will be gained into this phenomenon. An understanding of this effect is very important in predicting the types of minerals with which plutonium will be associated and, thus, its fate in the aqueous environment.

The extent and rates of sorption and desorption of Pu (IV) onto silica will be studied as a function of the ionic strength of the ambient solution. Initially, salt solutions of potassium perchlorate will be used at ionic strengths between 5×10^{-1}N and 1×10^{-3}N. Other ionic species commonly

found in natural waters will aid in the general study of the effect of the ambient solution composition on the sorptive process. This study should answer such questions as: a) Does the ionic strength influence the nature and size of the Pu (IV) species and, hence, the diffusion of Pu (IV) across the unstirred liquid layer? b) Do naturally-occurring cations compete with Pu (IV) for the silanol sites on the silica surface? c) Does the ionic strength cause a change in the silica surface which might influence sorption? d) Do naturally-occurring ions affect Pu (IV) in any way so as to influence its sorptive properties?

The rate of sorption (and desorption) will also be studied as a function of the rate of agitation of the silica-Pu (IV) system. This effect will probably be studied at two extremes, very slow and very high rates of agitation. A high rate of agitation may decrease the thickness of the unstirred film around the silica particles and thus increase the rate of diffusion of the Pu (IV) polymer to the silica surface. The rate of agitation may also affect the coagulation of Pu (IV) aggregates.

It is also planned to study the role that a few representative complexing agents might play in the sorption of Pu (IV) onto minerals.

REFERENCES

1. Industrial and Radioactive Waste Disposal, Hearings of the U.S. Congressional Joint Committee on Atomic Energy, Aug., 1959.

2. Morton, R.J., Status Report No. 4 on the Clinch River Study, USAEC ORNL-3409, Sept., 1963.

3. Cottrell, W.D., Radioactivity in Silt of the Clinch and Tennessee Rivers, USAEC ORNL-2847, Dec. 1959.

4. Sabo, J.J. and Bedrosian, P.H., Studies of the Fate of Certain Radionuclides in Estuarine and Other Aquatic Environments, PHS Publication No. 99-R-3, May, 1963.

5. Sayre, W.W., Guy, H.P. and Chamberlain, A.R., Uptake and Transport of Radionuclides by Stream Sediments, Geol. Survey Prof. Paper 433-A, 1963.

6. Garder, K. and Skulberg, O., Int. J. Air & Water Poll., 8, 229 (1964).

7. Mitchell, N.T. and Eden, G.E., J. Inst. Water Engrs., 16, 175 (1962).

8. McKay, H.A.C., "Alpha Emitters in Reactor Waste", in Atomic Energy Waste, E. Glueckauf, Ed., Interscience, N.Y. 1961.

9. Adamson, A.W., Physical Chemistry of Surfaces, Chap. XIII, Interscience, N. Y. 1960.

10. Rhodes, D.W., Soil Sci., 84, 465 (1957).

11. Christenson, C.W., et al, Sew. & Ind. Wastes, 30, 1478 (1958).

12. Jacobson, L. and Overstreet, R., Soil Sci., 65, 129 (1948).

13. Samartseva, A.G., Radiokhimiya, 4, 647 (1962).

14. King, E.L., Radiocolloidal Behavior of Neptunium and Plutonium. Adsorption of Plutonium (IV) at Trace Concentrations Onto Glass, USAEC MDDC-393.

15. Carniglia, S.C., Adsorption of Colloidal Plutonium by Glass, USAEC CN-2330, Nov., 1944

16. Haissinsky, M. et LaFlamme, Y., J. Chim. Phys., 55, 510 (1958).

17. Haissinsky, M. et Paiss, Y., J. Chim. Phys., 56, 915 (1959).

18. Okenden, O.D. and Welch, G.A., J. Chem. Soc., 653, 3358 (1956).

19. Grebenschchikova, V.I. and Davydov, Y.P., Radiokhimiya, 7, 191 (1965).

20. Lindenbaum, A. and Westfall, W., Int. J. Appl. Rad. Isotopes, 16, 545 (1965).

21. Taube, M., Plutonium, The Macmillan Co., N. Y. 1964.

22. Hindman, J.C., The Transuranium Elements, Seaborg, Katz and Manning, Ed's., Nat. Nuclear Energy Series, Vol. 14B, Paper 4.4, McGraw-Hill, 1954.

23. Kraus, K.A. and Dam, J.R., Ibid, Paper 4.14.

24. Hindman, J.C. and Ames, D.P., Ibid, Paper 4.2.

25. Kraus, K.A., Ibid, Paper 3.16.

26. Coleman, G.H., The Radiochemistry of Plutonium, National Academy Sciences-National Research Council, Sept., 1965.

27. Schubert, Jack, The Radiocolloidal Properties of Some Fission Products, USAEC AECD-1910 (1948).

28. Hindman, J.C., The Actinide Elements, Seaborg and Katz, Ed's., National Nuclear Energy Series, Vol. 14A, Chap. 9, McGraw-Hill, 1954.

29. Bensen, D.W., Review of Soil Chemistry Research at Hanford, USAEC HW-67201.

30. Schubert, J. and Conn, E., Nucleonics, 4, No. 6, 2 (1949).

31. Iler, R.K., The Colloid Chemistry of Silica and Silicates, Cornell University Press, Ithaca, N.Y., 1955.

32. Stanton, J. and Maatman, R.W., J. Colloid Sci., 18, 132 (1963).

33. Ahrland, S., and Grenthe, I and Noren, B., Acta Chem. Scand. 14, 7 (1960).

34. Talvitie, N.A. and Hyslop, F., Am. Ind. Hyg. Assoc. J., 19, 54 (1958).

35. Reichenberg, D., J. Amer. Chem. Soc., 75, 589 (1953)